PB-219 009

CHEMICAL COMPOSITION OF PARTICULATE AIR POLLUTANTS FROM FOSSIL-FUEL COMBUSTION SOURCES

L. J. Hillenbrand, et al

Battelle Columbus Laboratories

Prepared for:

Environmental Protection Agency

1 March 1973

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EPA-R2-73-216
March 1973

PB 219 009

on

CHEMICAL COMPOSITION OF PARTICULATE AIR POLLUTANTS FROM FOSSIL-FUEL COMBUSTION SOURCES

(Contract No. EHSD 71-29)

to

OFFICE OF RESEARCH AND MONITORING
ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NORTH CAROLINA 27711

March 1, 1973

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FINAL REPORT

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by

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BIBLIOGRAPHIC DATA SHEET

1. Report No. EPA-R2-73-216

2.

3. Recipient's Accession No. PB-219 009

4. Title and Subtitle
Chemical Composition of Particulate Air Pollutants from Fossil-Fuel Combustion Sources

5. Report Date March 1, 1973

6.

7. Author(s) L.J. Hillenbrand, R.B. Engdahl, and R.E. Barrett

8. Performing Organization Rept. No.

9. Performing Organization Name and Address
BATTELLE, Columbus Laboratories
505 King Avenue
Columbus, Ohio 43201

10. Project/Task/Work Unit No.

11. Contract/Grant No. EHSD 71-29

12. Sponsoring Organization Name and Address
EPA, Office of Research and Monitoring
NERC/RTP, Control Systems Laboratory
Research Triangle Park, North Carolina 27711

13. Type of Report & Period Covered Final

14.

15. Supplementary Notes

16. Abstracts The document reports the effect of effluent conditions and sampling techniques on the composition and amount of particulates measured in gases emitted from oil- and coal-fired combustion sources. Using an EPA sampling train and single-point sampling procedures, the changes in particulate catch produced by modification of that sampling apparatus and in sample-handling procedures were investigated. The effects of materials of construction, filter-media efficiency, sample drying and handling procedures, and sampling component temperatures on the mass and chemical composition of the collected material were determined. The major problems were associated with alterations in the form of sulfur compounds and the location of their collection in the sampling equipment. The principal conclusions concern the problems of sulfur oxides in the flue gases. Laboratory and field experiments indicate that some common conditions of impinger sample collection and handling can produce a significant increase in the material collected, by oxidation of a minor part of that absorbed SO2. Another source of sample alteration is the probe and and filter because of the effect of SO_3 in raising the dew point of the gases. The filter should be operated at well above 250°F: the SO_3 (H_2SO_4) can then be measured separately by the Shell-Thornton or equivalent method.

17. Key Words and Document Analysis. 17a. Descriptors

Gas Sampling
*Particulate
Air Pollution
*Chemical Analysis
Fossil Fuels
Electrostatic Precipitators
Combustion Products
*Sampling
Material Balance
Sulfur Oxides
Coal
Oils
Filtration
Materials Handling
Drying
Temperature
Dew

17b. Identifiers/Open-Ended Terms

Air Pollution Control
EPA Sampling Train
Stationary Sources
Materials of Construction

Details of illustrations in this document may be better studied on microfiche

17c. COSATI Field/Group 7A, 13B, 14B ib

18. Availability Statement Unlimited

19. Security Class (This Report) UNCLASSIFIED

20. Security Class (This Page) UNCLASSIFIED

21. No. of Pages 174

22. Price

TABLE OF CONTENTS

Page

ABSTRACT vi

Section

I. EXECUTIVE SUMMARY. I-1

OBJECTIVES . . . . -2

SCOPE. . . . . -2

SUMMARY AND CONCLUSIONS. . . . . -4

Sampling Apparatus and Procedures . . . . -7
Overall Particulate Compositions and Material Balances. . . . . -10
Sulfur Compounds. . . . . -13

SUGGESTED FUTURE WORK. . . . . -14

II. BACKGROUND II-1

GAS AND PARTICULATE COMPOSITIONS . . . . -1

Origins of Particulate Matter . . . . -4

Inorganic Particulate . . . . -5
Nucleated Material From Supersaturated Vapors . -7
Material Added by Physical or Chemical Adsorption. . . . . -11
Condensibles Originating by Chemical Reaction . -16

Conclusions Pertaining to Particulate Formation and Reactions in Flue Gases . . . . -20

Station 1: Ahead of Electrostatic Precipitator. -20
Station 2: After Electrostatic Precipitator . . -21
Station 3: External Filter at 220 F . . . . . . -22
Station 4: Plume of Impinger. . . . . -22

Sampling Train. . . . . -22

III. EXPERIMENTAL PROGRAM III-1

RESEARCH PLAN. . . . . -1

Phase I. State-of-the-Art Report. . . . . -1
Phase II. Plan Research Program . . . . -1
Phase III. Execute the Test Program . . . . . . -2

TABLE OF CONTENTS (Cont'd)

Section | Page

III. (Cont'd)

Experimental Equipment and Methods. III-4
  Multifuel Furnace Facility. . . . . -4
    Design Features . . . . -4
    The Multifuel Furnace . . . . -4
    Simulated Boiler/Economizer Section . . . . -7
    Electrostatic Precipitator. . . . . -7
    Stack . . . . -8
    Operational Characteristics . . . . -8
    Analytical Methods. . . . . -13
  C, H, N Analyses. . . . . -13
  Wet Chemical Analysis for S . . . . -13
  Goksøyr-Ross Procedure for SO_3 and SO_2. . . . . -13
Experimental Details and Results. . . . . -15
  Initial Trials. . . . . -15
  Experimentation Using Multifuel Furnace, Coal-Fired Operation. . . . . -24
  Field Experiments . . . . -39
    Effect of Drying Conditions . . . . -39
    Experiments at Edgewater Power Station. . . -41

IV. DISCUSSION OF RESULTS IV-1
  OVERALL COMPISITIONS AND MATERIAL BALANCES . . . . -1
  SAMPLING APPARATUS AND PROCEDURES. . . . . -14
    Probe . . . . -14
    Filter. . . . . -15
    Impinger. . . . . -17
  Sampling Train Modifications. . . . . -17
    Simultaneous Sampling . . . . -17
    Use of the G/R Coil in Particulate Sampling . . -18
    Field Trials. . . . . -19
  Sample Handling . . . . -21
  Suggested Sampling Procedures . . . . -23
  Inorganic Ash (less S). . . . . -25
  Sulfur Compounds. . . . . -27

V. RECOMMENDATIONS FOR FUTURE WORK. V-1

VI. ACKNOWLEDGEMENTS VI-1

TABLE OF CONTENTS (Cont'd)

Section — Page

III. (Cont'd)

Experimental Equipment and Methods. III-4
  Multifuel Furnace Facility. . . . . -4
    Design Features . . . . -4
    The Multifuel Furnace . . . . -4
    Simulated Boiler/Economizer Section . . . . -7
    Electrostatic Precipitator. . . . . -7
    Stack . . . . -8
    Operational Characteristics . . . . -8
    Analytical Methods. . . . . -13
  C, H, N Analyses. . . . . -13
  Wet Chemical Analysis for S . . . . -13
  Goksøyr-Ross Procedure for SO_3 and SO_2. . . . . -13
Experimental Details and Results. . . . . -15
  Initial Trials. . . . . -15
  Experimentation Using Multifuel Furnace, Coal-Fired Operation. . . . . -24
  Field Experiments . . . . -39
    Effect of Drying Conditions . . . . -39
    Experiments at Edgewater Power Station. . . -41

IV. DISCUSSION OF RESULTS IV-1

OVERALL COMPISITIONS AND MATERIAL BALANCES . . . . -1

SAMPLING APPARATUS AND PROCEDURES. . . . . -14
    Probe . . . . -14
    Filter. . . . . -15
    Impinger. . . . . -17
  Sampling Train Modifications. . . . . -17
    Simultaneous Sampling . . . . -17
    Use of the G/R Coil in Particulate Sampling . . -18
    Field Trials. . . . . -19
  Sample Handling . . . . -21
  Suggested Sampling Procedures . . . . -23
  Inorganic Ash (less S). . . . . -25
  Sulfur Compounds. . . . . -27

V. RECOMMENDATIONS FOR FUTURE WORK. V-1

VI. ACKNOWLEDGEMENTS VI-1

TABLE OF CONTENTS (Cont'd)

APPENDICES

APPENDIX A
CONVERSION OF SO_3 to H_2SO_4

APPENDIX B
WET CHEMISTRY METHODS FOR SULFUR COMPOUNDS

APPENDIX C
FILTER EFFICIENCY MEASUREMENT

APPENDIX D
FIELD TEST SAMPLES FROM OTHER EPA CONTRACTORS

APPENDIX E
KINETICS OF SO_2 OXIDATION

APPENDIX F
REFERENCES

LIST OF FIGURES

Page

Figure 1. Locations at Which Collected Samples May Reflect Particulate-Forming Reactions. II-3
Figure 2. Typical Distribution of Deposits in Oil-Fired Boilers. II-6
Figure 3. Relation of Dewpoint and SO_3 Content of Combustion Gases to Sulfur Content of Oil II-10
Figure 4. Variation of Dewpoint With H_2SO_4 Content for Gases Having Different Water-Vapor Contents. II-11
Figure 5. Dewpoint as a Function of H_2SO_4 Concentration. . . . II-12
Figure 6. Log_{10} Versus Log_{10} P/K for Simple Languir Model . . II-14
Figure 7. EPA Particulate Sampling Train II-23
Figure 8. Schematic Representation of Multifuel Furnace System III-5
Figure 9. Battelle Multifuel Furnace III-6
Figure 10. Time-Temperature Profile Typical of Oil Firing . . . III-9
Figure 11. Time-Temperature Profile Typical of Coal Firing. . . III-10

TABLE OF CONTENTS (Cont'd)

FIGURES (Cont'd)

Page

Figure 12. Optical Emission Spectrography III-11

Figure 13. Schematic Representation of OES Principle. III-11

Figure 14. X-ray Emission Spectrometry (Fluorescence, XRF). . . III-12

Figure 15. Schematic Representation of XRF Principle. III-12

Figure 16. Goksøyr-Ross Coil. III-14

Figure 16.1. Goksoyr-Ross Procedure III-16

Figure 17. Schematic View of Sample Port P-1. . . . . III-17

Figure 18. Flow Chart of Analytical Procedure for Particulate Samples from Coal-Fired Operation of Laboratory Furnace. III-27

Figure 19. Schematic Representation of the Experimental Apparatus for Investigation of SO_2 and SO_3 . . . . . III-36

Figure 20. Flow Sheet for Procedures in Treatment and Analyses of Stack Emission Samples III-54

Figure 1C. Sketch of Sampling Arrangements. C-2

Figure 2C. Particle Size Distribution C-3

LIST OF TABLES

Table A. Study of the Influence of Sampling Procedures on the Chemical Composition of Particulate (Flow Sheet for the Iterative Program) I-5

Table 1. Typical Exhaust-Gas Composition From Coal-Fired Boiler II-2

Table 2. Initial Trials, Results from Oil-Fired Laboratory Burner III-18

Table 3. Comparison of Glass and Quartz Filter Materials. III-20

Table 4. OES Analyses (± 50%) for Impurities in Glass and Quartz Filter Materials. III-21

Table 5. Effect of Drying Treatments Upon Apparent Mass of Particulate Samples. III-23

Table 6. Coal Analyses in Multifuel Furnace Facility. III-24

Table 7. Plan for a Series of Experiments Particulate Collections from the Laboratory Coal-Fired Furnace System III-26

TABLE OF CONTENTS (Cont'd)

TABLES (Cont'd)

Page

Table 8. Analytical Data for Particulate Collection from Coal-Fired Laboratory Burner III-29

Table 9. Comparison of C, H, N Contents Following Extraction of Filter Portions with Benzene and Aqueous Acid III-33

Table 10. Oxidation of SO_2 During Sampling of Stack Gases from the Multifuel Furnace Under Various Conditions. . . III-37

Table 11. Effect of Drying Conditions on Sample Weights. III-40

Table 12. Investigation of Oxidation State for Sulfur Oxides Retained in Several Variations of the Particulate Train. III-42

Table 13. Comparison of the Sulfur Contents of Impinger Water Stored in Different Ways III-45

Table 14A. General Data for Runs 49, 50, 53, 55, 56. . . . . III-47

Table 14B. Distribution of Chemical Elements Among the Portions of Particulate Catch With a Double Filter III-48

Table 14C. Distribution of Chemical Elements Among the Portions of Particulate Catch With a Single Filter Arrangement III-50

Table 15. General Sample Descriptions, Treatments, and Analytical Methods for Characterization of Stack Samples Taken at Lorain, Ohio III-55

Table 16. Derived Quantities and Trial Material Balances IV-2

Table 17. Summary of C, H, N Analyses for Particulate Samples. . . IV-7

Table 18. Trial Material Balances for Particulate Samples, Edgewater Power Station. IV-9

Table 19. C, H, N Analyses of Dry Material Samples from Edgewater Power Station. IV-11

Table 20. Impinger and Probe Catch for Single and Double Filter Experiments, Lorain IV-22

Table 21. Comparison of Calculated Solubilities for SO_2 in Water with Those Found in Run 41. . . . . IV-28

Table 22. Estimated Concentrations for Sulfite Species in Aqueous Solutions. IV-29

Table 1C. Comparison of Quartz-Fiber Filter and MSA 1106B Glass Fiber Filters. C-1

Table 1D. Chemical Analyses of Fractions of 4 Stack Samplers . . . D-2

ABSTRACT

The abatement of sources of particulates emitted to the ambient air is requiring a greatly increasing national effort to try to achieve the established standards of ambient air quality. The results of this effort cannot be achieved most economically if reliable methods are not available to measure the particulate emissions. The project was conducted to determine the effect of effluent conditions and of sampling techniques on the composition and amount of particulates measured in the gases emitted from oil and coal-fired combustion sources. These effects are becoming increasingly important as the efficiency of practical collection devices approaches 100 percent. Then any extraneous effects on the accuracy of particle measurements loom rapidly in importance whereas, heretofore, these effects were relatively small in measurements taken on collection equipment of low or moderate efficiency.

Since no absolute or referee methods for collection of valid samples of particulate exist for this program, the EPA sampling train chosen as the best available method for particulate collection. An investigation was made of the changes in particulate catch produced by modification of that sampling apparatus and in sample-handling procedures. Such comparisons were made using single-point sampling procedures instead of conventional traversing since emission testing was not a direct objective of this work. For this reason, the comparisons of individual results on the basis of loading per unit volume of gas are not necessarily meaningful.

This project began with particulate measurements in the gases from a laboratory furnace capable of burning either residual oil or pulverized coal. The sampling train used was the EPA train consisting of a heated probe, heated filter, and chilled impingers. After the chemical characteristics of the particulate samples had been carefully examined under these laboratory conditions the sampling train and some modifications of it were applied to the gases from a pulverized-coal-fired power plant.

For the evaluation of control technologies, any alteration in the amount or composition of materials collected in the sampling train may result in erroneous conclusions regarding the process operation and/or chemistry and is therefore undesirable. Experimental work was conducted to determine the effects of materials of construction, filter-media efficiency, sample drying and handling procedures, and sampling component temperatures on the mass and chemical composition of the collected material. In all cases, an alteration of 1 percent or greater was considered as a guideline for the maximum change acceptable for control technology development studies. After a series of screening experiments, it was concluded that the major problems were associated with alterations in the form of sulfur compounds and the location of their collection in the sampling equipment. More detailed studies were then focused on the sulfur oxides and their effect on the collected sample.

The principal conclusions of this research revolve around the problems of sulfur oxides in the flue gases.

If the sulfur content of the fuel is low, say below 0.5 percent, then the concentration of SO_2 and SO_3 produced by combustion is relatively low and sample alteration from acid condensation and reaction may be small. However, where many practical fuels contain six or more times that much sulfur (3 percent sulfur and more), alterations in the mass reactions can be large. About 10 percent of the total SO_2 in the gas stream was found to be retained by the impingers. Laboratory and field experiments carried out under this program indicate that some common conditions of impinger sample collection and handling can produce a significant increase in the material collected by oxidation of a minor part of that absorbed SO_2.

Another potential source of sample alteration can occur in the probe and filter because of the effect of SO_3 in raising the dew point of the gases. The dew point of flue gases from moderate and high-sulfur fuels ranges from 250 to 300 F. In these experiments a filter operated at 250 F caught over 41 percent of the total sulfur caught. Operated at 400 F, the filter caught only 8 to 24 percent of the total sulfur caught. Thus, if it is necessary to determine the actual distribution of sulfur species in the flue gas, it is recommended that the filter be operated well above 250 F. The SO_3 (H_2SO_4) which is also potential particulate in the flue gases can then be measured separately by the Shell-Thornton or equivalent method. Usually about 1 or 2 percent of the sulfur oxide in the gases is present as sulfur trioxide (or H_2SO_4) in the typical moist gases at or near the acid dew point.

Regardless of the type and configuration of probe-filter combination used in particulate sampling, there is always a possibility that the filter will fail and lose part of the sample. When testing high-efficiency equipment, such a loss may cause serious error but be visually undetectable. Since measurement of particulate after high-efficiency devices requires sampling times of several hours or more, it appears reasonable to include a backup filter as a precaution against having to discard the entire test at a later time when the weighing results are known. While impingers may provide such a backup, their efficiency for submicron particles is questionable and the chemical reactions found to occur will complicate the data. A second heated filter as backup will incur less uncertainty.

I. EXECUTIVE SUMMARY

OBJECTIVES

SCOPE

SUMMARY AND CONCLUSIONS

  Sampling Apparatus and Procedure

  Overall Particulate Composition and Material Balances

  Sulfur Compounds

SUGGESTED FUTURE WORK

CHEMICAL COMPOSITION OF PARTICULATE AIR POLLUTANTS FROM FOSSIL-FUEL COMBUSTION SOURCES

by

L. J. Hillenbrand, R. B. Engdahl, and R. E. Barrett

I. EXECUTIVE SUMMARY

In the current national effort to improve air quality, one of the most difficult tasks is to reduce the level of suspended particulates in the densely populated metropolitan and industrial areas. A 1975 primary goal for particulates in the atmosphere has been set at only 75 μg grams per cubic meter, annual geometic mean. Many urban areas now have a geometric mean level well over 100 μg. These measured levels include all suspended particulates, liquid or solid, as collected by glass-fiber filters on high-volume air samplers. A major effort is underway to abate most U. S. man-made sources of these suspended particulates.

In this program of abatement of these myriad particulate sources it is important to be able to measure their emissions accurately so that the magnitude and rate of improvement can be reliably gaged, and the measurement should logically include those emitted substances which will become ambient particulates when measured at ambient air conditions.

However, while the high-volume ambient air sampler indiscriminately samples suspended solids and liquid droplets as particulates in the atmosphere, the abatement of their sources requires that the type of particulate can be identified and not just lumped together. There are two reasons for this. In the first place not all particle collectors will collect all types of particles. Thus, different methods of abatement may be required for various particulates. Also, if liquid and solid particulates are combined during the process of sampling, there is the possibility that chemical reactions will occur which could affect the accuracy of the measurement. Hence, this project has been directed toward examination of the effect of the methods used in sampling particulates from fossil-fuel-fired sources on the chemical composition of those particulates.

OBJECTIVES

(1) To examine the chemical interactions that occur during sampling and which influence the estimates of particulate emissions from fossil-fuel-fired combustion sources.

(2) To detect the influence that the operation of abatement equipment such as electrostatic precipitators for particulate control has on the nature of the particulate sampled and emitted.

(3) To evaluate techniques for measurement of particulate loadings in the inlet and outlet streams from such control equipment.

SCOPE

Historically, EPA has proposed that particulate matter be defined as all solids and those condensible materials which are liquid at standard conditions of 1 atmosphere and 70 F, excepting uncombined water. Present methods for sampling and weighing particulate emission do not necessarily reflect particulate levels as thus defined. For many years the predominant accepted methods for measuring fly ash used only the dry filtration or a combination of dry filtration and wet impingement. The former fails to collect condensible materials that may exist as vapors at the filter temperature but may immediately become liquid particulates at ambient temperatures, and the liquid impingers used on some particulate trains may generate particulate by chemical reaction in the impingers, thus producing erroneous data on particulate emission levels.

Also, the knowledge of how conditions before and after particulate emission control devices (such as electrostatic precipitators and wet scrubbers) may influence particulate measurements is incomplete. As the application of these control devices is becoming more widespread, it is necessary that their influence on particulate emission measurements be established by evaluating present or proposed sampling methods on operating units. Hence, new or modified sampling methods may be required to produce a measure of particulate loading that is consistent with the above definition for the evaluation of particulate emission control devices.

Since no absolute referee methods for collection of valid samples of particulate exist for this program, a commercially available version of the EPA sampling train was chosen as the best available method for particulate collection and an investigation was made of the changes in particulate catch produced by modifications of that sampling apparatus and in the sample-handling procedures. Such comparisons were made using single-point sampling procedures instead of conventional traversing since quantitative emission testing was not a direct objective of this work. For this reason the comparisons of individual results on the basis of loading per unit volume of gas are not necessarily meaningful.

Experiments were first run sampling gases from the laboratory furnace to determine the chemical composition of particulates caught in the various parts of the sampling train. Then the effect of temperature on that sample composition was explored. Different filter materials were tried because variations in chemical composition of glass filters caused serious uncertainties during analysis of the filter catch. A novel quartz filter material was tried and adapted to the requirements of this program.

The sampling apparatus was then taken to a coal-fired power plant where the effect of sulfur oxides on particulate composition was investigated. The influences of sample-handling procedures on sample accuracy were also studied.

Most of the sampling was done on coal-fired operations because most particulate control equipment installations are on coal-fired plants. The research nature of the objectives made it possible to conduct a major part of the sampling program using the Battelle Multifuel Furnace burning either residual oil or coal. Samples collected from this furnace were used to acquire background for further sampling operation under the more difficult field sampling conditions at a power plant.

As work continually underscored the problems associated with SO_2 oxidation and H_2SO_4 condensation from wet combustion gases, special attention was given to this aspect of the problem. Although it must be recognized that SO_2 dissolved in water mist in the atmosphere also oxidizes to create sulfate particulate, and the SO_3 combines with water to form acid mist, the need to measure them separately still remains.

Reliable field methods for handling SO_2/SO_3 mixtures in the presence of alkaline materials are needed before the special problems associated with scrubbers can be investigated properly only in the field For this reason, the investigation of such equipment was delayed and has not been included in this phase of the investigation.

The effects of electrostatic precipitators on particulate were examined both in the gases from the Battelle Multifuel Furnace and in the field at a coal-fired power plant, the Edgewater Station, Lorain, Ohio.

The evolution of sampling and sample-handling procedures has included trials of a number of variations that were planned to help assess the importance of problematic aspects as they were recognized. These trials have been used to evolve a concept for improved procedures that may be useful in specifying the emissions that characterize fossil-fuel combustion in modern practice.

Table A summarizes the steps followed in the iterative investigation of sampling techniques.

SUMMARY AND CONCLUSION

Major problems associated with the sampling and measurement of particulate emissions from fossil-fuel-fired plants either to determine flue gas composition or to evaluate the performance of particulate control apparatus are:

(1) Generation of sulfate by oxidation of SO_2 in the impingers. This is also a potential problem in the probe and filter.

(2) Condensation of H_2SO_4 or adsorption of SO_2 in the probe or filter.

TABLE A. STUDY OF THE INFLUENCE OF SAMPLING PROCEDURES ON THE CHEMICAL COMPOSITION OF PARTICULATE
(FLOW SHEET FOR THE ITERATIVE PROGRAM)

BATTELLE MULTIFUEL FURNACE				
Initial Trials, Oil-Fired	First Series, Coal-Fired	Second Series, Coal-Fired	Field Trials Edgewater Power Station Coal-Fired	Items Investigated
------------------	probe material and temperature Tables 7, 8	-------------------	------------------------	Probe Catch IV-5, 1 to 15
filter material and temperature Table 2	temperature effects; comparative data for quartz Tables 7, 8	-------------------	single and double filters; temperature Tables 12, 14	Filter Catch IV-5, 15 to 16
-----------------	-------------------	acidity effects; 4x"wet" impingers in series Table 10	acidity effects; 4x"wet" impingers in series Table 12	Impinger Catch IV-17
----------------	coil used without frit; before and after filter; acidity removal Tables 7, 8	comparison to impinger catch, in parallel Table 10, Figure 19	before impingers; comparison to impinger catch Table 12	G/R (Shell Coil Use IV-17-20
----------------	distribution among portions of catch; acidity and temperature effects Table 8	comparison of G/R coil and impinger catches; acidity and oxidation effects Table 10	comparison of G/R coil and impinger catches Table 12	Sulfur Oxides IV-17 to 24, 27-33
filter catch composition Table 2	probe, filter, and impinger portions - weight and composition Table 8	-------------------	probe, filter, and impinger portions - weight and composition Table 14	Ash Composition IV-25 to 27
water catch; drying conditions Table 5	analytical accounting of total catch - uncertainties Table 8	-------------------	analytical accounting of total catch - drying conditions Tables 11,12,14	Total Catch IV-1 to 14
XRF and OES of filter catch; sample drying Tables 2, 5	C,H,N, and OES, XRF analyses of aliquots, all portions Table 7,8, Figure 18	individual analyses for 4 impingers in series; organic and aqueous washings Table 10, Figure 19	aliquot collection OES and XRF analyses; all portions, dry, aqueous, and organic layers Table 11,12,13,14,15 Figure 20	Sampling Procedure and Analysis IV-17 to 24

(3) Fractionation of the composite of ash, sulfur oxides, and organic components during passage of the particulate through the sampling apparatus.

(4) Retention of water, especially in those portions of the catch that include free sulfuric acid.

(5) Probable loss of identity of organic materials that are collected simultaneously with the sulfuric acid.

The first two of these have received most of the attention in this program. The work done is regarded as the first phase of the investigation that is needed to establish the effects of control apparatus on particulate concentration levels and composition. Subsequent phases should be directed toward the research and areas discussed in the section entitled, "Recommendations for Future Work".

The particulate is identified as a mixture of

(1) Fly ash: solid particulate, mainly minerals, partially reacted with the sulfur and oxygen in the stack gas,

(2) Sulfur: present as free sulfuric acid, absorbed and adsorbed, and combined as sulfate and sulfite,

(3) Organic material: condensates probably ranging from volatile materials to high-molecular-weight materials such as the benzpyrenes and metal-organic complexes,

(4) Water: combined as hydrate water in the inorganic catch and water retained by the free sulfuric acid,

and the experiments were planned as an investigation of the importance of each and the problems that they contribute to the measurements of flue gas components.

In attempting to make material balances of the metal and sulfur in compounds in the flue gases, that is, to account for all of the catch by chemical analysis, uncertainties of sampling and analyses were revealed in spite of the special attention given to such problems in this program. In turn, these uncertainties are a reflection of the limitations that should be recognized in comparing any two sets of data. The uncertainties are experienced especially in assessing the metal analyses for the impinger portions. Here, the greatest mass of the impinger catch is due to sulfur oxides and only very small amounts of individual metal compounds are found. Collectively, these metal compounds appear to account for 1 or 2 percent of the total impinger catch, but such estimates are best regarded as maximum estimates rather than typical values.

Because the small amounts of sample and the low concentrations of most elements in both blank and sample, there are large analytical uncertainties in these impinger portions. The elemental analyses for these portions were obtained as an expression of the levels of concentration found for each element and were intended to reveal any tendencies for the heavier (toxic) metals to be carried through the filter as a result of their chemical forms. Since both blank and sample are subject to large analytical uncertainties in these impinger portions the analyses are given, except for a few of the major elements, without correction for blank and as such, represent maximum values that may be assigned to each element. Probe and filter analyses are in general not subject to this same degree of uncertainty except where trace amounts are reported.

The work that has been done falls roughly into the subject areas

- Sampling apparatus and procedures
- Overall particulate and compositions
- Sulfur oxide investigations

and the conclusions are grouped under the above headings.

Sampling Apparatus and Procedures

1. Three filter materials were considered: a silver filter, MSA Glass 1106 BH, and Tissuquartz QAO 2500. Only one run was made using the silver filter because large areas of visible stain on the filter after the run indicated that the anticipated reaction of the silver with the H_2SO_4 vapors had indeed occurred. At the usual moist stack conditions SO_3 does not exist as a gas but is largely hydrated chemically to H_2SO_4 vapor. In most cases the separation of the filter catch from the filter itself is not practical. Therefore, the chemical analyses of the catch have highest precision and sensitivity as the filter material becomes more precisely defined. The silver filter is best from this standpoint because it can be dried to constant weight

easily and impurity elements are of little consequence in most cases. However, the reactivity of the silver with sulfur compounds led to a preference for the pure and relatively inert quartz filter material.

2. The filter temperature appears to affect significantly the composition of the filter catch. Thus, at 400 F the filter retained substantially less sulfur oxides than a comparable filter at 250 F. This is no surprise if one recalls earlier research showing that the acid dewpoint of fossil-fuel flue gases is often lower than 300 F. The greater amount of sulfur oxides found on the cooler filter is interpreted to mean: a. that a considerable portion of the sulfur collected on that filter might have resulted from both condensation and reaction of the particulate with the SO_2 and SO_3, and b. that the condensation and consequent reaction is favored at the lower temperature. Oxidation of SO_2 is estimated to be minor.

3. The impingers also retain on the order of 10 percent or more of the total SO_2 as measured by the G/R coil* procedure(1) so that accurate sulfate estimates from impinger catches require inhibition of SO_2 oxidation during collection, sample storage and evaporation, and analysis. The experimental results appear to require use of a separate train, such as the G/R train, for accurate sulfur oxide measurement rather than analyzing the impinger liquid for this purpose.

4. The G/R procedure is easy to use and provides reproducible results. EPA has supported a demonstration of the absolute accuracy of the method for stack gas conditions. (Walden Labs. Contract No. CPA 22-69-95, Final Report, June, 1971.)

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* (Goksøyr-Ross; also called Shell Method).

(1) References in Appendix F.

5. The G/R coil inserted between filter and impingers collected a substantial portion of the total H_2SO_4 found in that run and was far more effective than a cooler second filter tried in its place in one experiment. In the experiment with the coil, if it is assumed to be as efficient as has been claimed, the sulfate found in the impingers of that run would seem to have been formed by oxidation in the impingers;

6. When two filters were used in series, the mass loading of the second filter was largely due to sulfur oxides retained there. The mass of fly-ash oxides on the second filter, excluding sulfur oxides, was small and the analyses for individual elements were subject to large uncertainties.

7. The high chromium and nickel contents of the catches, collected in the metal probes present evidence of the accumulation of corrosion products in the probe portion and, to some degree, in the filter portion at 250 F. Sulfur oxide retention by the metal probes was slightly higher than with a quartz probe, which may be a reflection of the increased reactivity of the catch due to those corrosion products.

8. On the basis of the observations to date, a sampling procedure for examination of the performance of particulate control equipment might be as follows:
   (a) Use a glass probe and quartz filter media with probe and filter at 400 F or higher to minimize condensation of SO_3 or reactions of sulfur dioxide in the sampling system.

   (b) Use a backup quartz filter media at 400 F or higher to prevent loss of sample if the first filter fails.

(c) Determine total SO_2 and SO_3 in the gas phase by a procedure, such as that of Goksøyr-Ross, operated simultaneously with the particulate collection.

(d) Use special collection trains for components such as PNA and certain hazardous metals present in relatively small concentrations. These trains would be adapted to the most suitable absorption or reaction condition for efficient collection of the component concerned.

(e) Attempt material balance by the use of a sufficient scope of analytical methods so that the entire mass of catch is indentified according to its chemical characteristics.

Overall Particulate Compositions and Material Balances

9. The assignment of definite oxide compositions to each of the chemical elements (found analytically) makes possible trial material balances and these balances show substantial deviation from 100 percent in some cases. The uncertainties may be due to the assumption of a definite oxide composition. However, it is more probable that the uncertainties arise from sampling and sample-handling procedures as much as from the inherent analytical difficulties.

10. The ratios of abundance of a pair of elements frequently are not the same in all portions of a catch, and these variations in abundance probably reflect differences in composition for particles of different size, as well as the presence of unburned coal in the particle and reactions with the gas phase as the mixture cools.

11. Analytical results show a varying Si/Al ratio for probe samples, probably because the Si and Al are contributed by both fly ash and coke having different Si/Al ratios.

The experimental Si/Al ratios for pairs of probe samples taken near a precipitator varied with the location as shown

Run	Date	Location	Si/Al Mass Ratio
49	10/6/71	E.P. inlet	3.0
50	10/6/71	E.P. outlet	20.0
55	10/8/71	E.P. inlet	0.31
56	10/8/71	E.P. outlet	2.1

These ratios were substantially greater for samples collected at the precipitator outlet than for those collected at the inlet.

12. For the samples obtained from firing coals, only the elements Na, K, Mg, Al, Ca, Fe, S, and presumably O and Si are present in the dry catch in significant amounts relative to the total mass of the particulate.

13. A number of heavy elements are present in amounts that are insignificant compared to the total mass of particulate, but which may need to be considered individually for their toxicity contributions.

    The total mass of elements found by chemical analysis, but excluding sulfur, indicates that the precipitator at the Edgewater Power Station removed 99.5 percent or better of the relatively coarse material caught in the probe and about 96 to 97 percent of the filter-catch portion.

14. Substantial percentages of both probe and filter catch material are composed of sulfur compounds and these percentages are greater in the precipitator outlet streams than in the inlet streams. The reasons for this are not yet determined.

15. The inorganic ash portion is distributed differently among probe, filter, and impinger than is the sulfuric oxide portion. In the runs made using the Battelle Multifuel Furnace, less than 2 percent of the ash was found by chemical analysis in the impinger, whereas between 6 and 85 percent of the sulfur oxide catch was found there. Other results obtained from samples collected at Edgewater Power Station show substantially smaller percentages of ash in the impingers. Thus, the mass distribution of the catch usually does not correspond to the distribution of any single component of the particulate.

16. The composition of the total catch varies too much to permit calculation of meaningful averages, but typical compositions for coal-burning operation based on these trial applications of the EPA train and its modifications would be:

	Battelle Multifuel Furnace, precipitator inlet[(a)]	Full-Scale Power Plant	
		Precipitator inlet	Precipitator outlet
Inorganic ash (less sulfur), wt percent	66	72	37
Sulfur, as H_2SO_4, wt percent	31	12 to 18	63
Carbon (coke or organics), wt percent	3	9 to 17	not determined

(a) Average for all runs, dry basis.

Thus, on the downstream side of precipitators, the sulfate can constitute a major portion of the material collected in the probe, on the filter, and in the impingers.

Sulfur Compounds

A considerable part of the experimentation was devoted to examination of the influence that the apparatus and conditions used for sampling can have on the sulfur oxide content of the catch. For this purpose, the SO_2 contents of samples were examined for several experimental sampling arrangements. In the temperature range below 400 F, essentially all SO_3 exists in wet-gas mixtures as H_2SO_4 and the terms SO_3 and H_2SO_4 are used interchangeably. Analytical determinations were made of SO_2, sulfate, and total sulfur (as sulfate) where appropriate. The conclusions were as follows:

17. The sulfur contents of the probe and filter portions were variable and it was not possible to estimate how much of the sulfur found in these portions was due to reaction of the collected solid with H_2SO_4 condensed from the gas phase or to SO_2 physically or chemically adsorbed during sampling. The total sulfur is probably a combination of sulfur oxide retention by such reactions plus sulfur that had already become incorporated into the particulate prior to sampling.

18. A relatively large amount of SO_2 is dissolved and retained in the impingers and the oxidation of only a minor fraction of that SO_2 would account for the sulfate formation. Kinetic calculations indicate that SO_2 oxidation in the impinger catches may be more serious during the typical periods of storage and analysis of the samples than is the oxidation during the 40-minute sampling time.

19. The formation of sulfate in impinger samples by oxidation of SO_2 was indicated by the observations that (a) when extra wet impingers were added to the sampling train, as much sulfate was found in the third and fourth impingers as in the first two; (b) more sulfate was found in the

impingers than in a G/R coil operated simultaneously; (c) considerable sulfate was found in the impingers operated in series with a G/R coil.

20. The sulfate analyses on any stored water sample collected in the field should be made on aliquots stored in completely filled bottles to avoid oxidation during storage and transportation of samples. Flushing of the sample with inert gas before sealing for storage is recommended.

21. As expected, pH has an important bearing on the process in the impingers. Increase of impinger pH to 5.5 increased both the SO_2 retained and the SO_3 found. The rise in SO_3 is believed good evidence for oxidation of the increased amounts of SO_2 retained in the impingers. Lowering of pH to 1.1 to 1.5 caused a decrease in SO_2 retained and the anticipated decrease in SO_3 was not found. Further work is needed on this matter. Approximate calculations of SO_2 solubility in strong acid at 0.1 N concentration indicate that total sulfite concentrations may be reduced by about one-half as compared with that for H_2O solvent.

SUGGESTED FUTURE WORK

Areas for further research all relate to the observation that some fractionation of particulate can occur in the particulate-control apparatus as well as in the furnace and boiler itself, and studies will be needed to establish a basis for measurement of control for each of the important classes of material. Among these areas for further research are

(1) Practical means for field sampling and analysis of total SO_3 content

(2) Sampling and analysis of small particles that may penetrate the filter

(3) Sampling and analysis of anions, especially halides, nitrates, and carbonates

(4) Study of the chemical state of selected heavy metals and identification of sampling difficulties for each, especially for Hg, Ba, Sb, Pb, As

(5) Study of special sampling conditions that are generated by scrubber-type particulate-control apparatus

(6) Demonstration of a valid sampling method for the evaluation of particulate-control-equipment efficiencies for specific effluent-gas components.

Conceivably, these studies will identify methods to supplement the existing sampling train, and these must be tried under comparative conditions in industrial applications where particulate and emission-control equipment is used. In this connection, the special problems generated by the use of scrubber-type control apparatus should be studied immediately so that the observations may be used to guide the other research areas discussed here.

II. BACKGROUND

GAS AND PARTICULATE COMPOSITIONS
- Origins of Particulate Matter
  - Inorganic Particulate
  - Nucleated Material From Supersaturated Vapors
  - Material Added by Physical or Chemical Adsorption
  - Condensibles Originating by Chemical Reaction
- Conclusions Pertaining to Particulate Formation and Reactions in Flue Gases
  - Station 1: Ahead of Electrostatic Precipitator
  - Station 2: After Electrostatic Precipitator or Stack
  - Station 3: External Filter at 220 F
  - Station 4: Plume of Impinger
- Sampling Train

II. BACKGROUND

GAS AND PARTICULATE COMPOSITIONS

The inclusion of both solid and liquid materials in the definition of particulates (page I-2) makes necessary a careful consideration of the origins of the particulate matter that is collected and of the influences that the sampling methods may have on this material. Of especial concern are those particulates that may form by chemical reaction and condensation either in the boiler and stack portions of the power plant (so that the total collection may vary as a function of sampling location) or in the sampling train during particulate collection. All these become even more significant as trends in the control of pollutant emissions reduce the upper limits of permissible quantities of material.

In order to consider in more detail the chemical and physical interactions that may occur between the gaseous and particulate components of the exhaust gases, it is convenient to select for quantitative examination a typical gas composition that may be produced by a power plant, as shown in Table 1. A similar set of concentrations can be described for an oil-fired plant. The major difference for oil firing would be a substantially higher H_2O/CO_2 ratio and lower fly-ash loadings. However, the above gas composition is sufficient for consideration of reactions that might form particulates.

Several combinations of sampling points and sampling train configurations should also be included in consideration of particulate-forming reactions. Figure 1 shows three sampling points that should be considered. These points are

Point 1. Ahead of the electrostatic precipitator (assumed gas temperature of 400 F)

Point 2. After the electrostatic precipitator (assumed gas temperature of 300 F)

Point 3. In the plume after dilution to 70 F.

TABLE 1. TYPICAL EXHAUST-GAS COMPOSITION FROM COAL-FIRED BOILER

Component	Concentration: Volume percent	Concentration: g/m^3 (a)	Relative Importance(b)
H_2O	4.0	30	0.02
CO_2	15.0	273	0.002
Fly ash before precipitator		9.16 (4 gr/ft^3)	--
Fly ash after precipitator		0.458 (0.2 gr/ft^3)	-- --
NO	0.050	0.63	0.8
SO_2	0.20	5.3	0.1
SO_3	0.0030 (30 ppm)	0.10	4.5
Hydrocarbons	(0.0010)	<0.1	>50.

(a) At 70 F, 1 atmosphere.

(b) Values show approximate percentage of the total amount of each component in the flue gases that, if collected as particulate would increase the measured loading by 1 percent (based on fly ash after the precipitator.

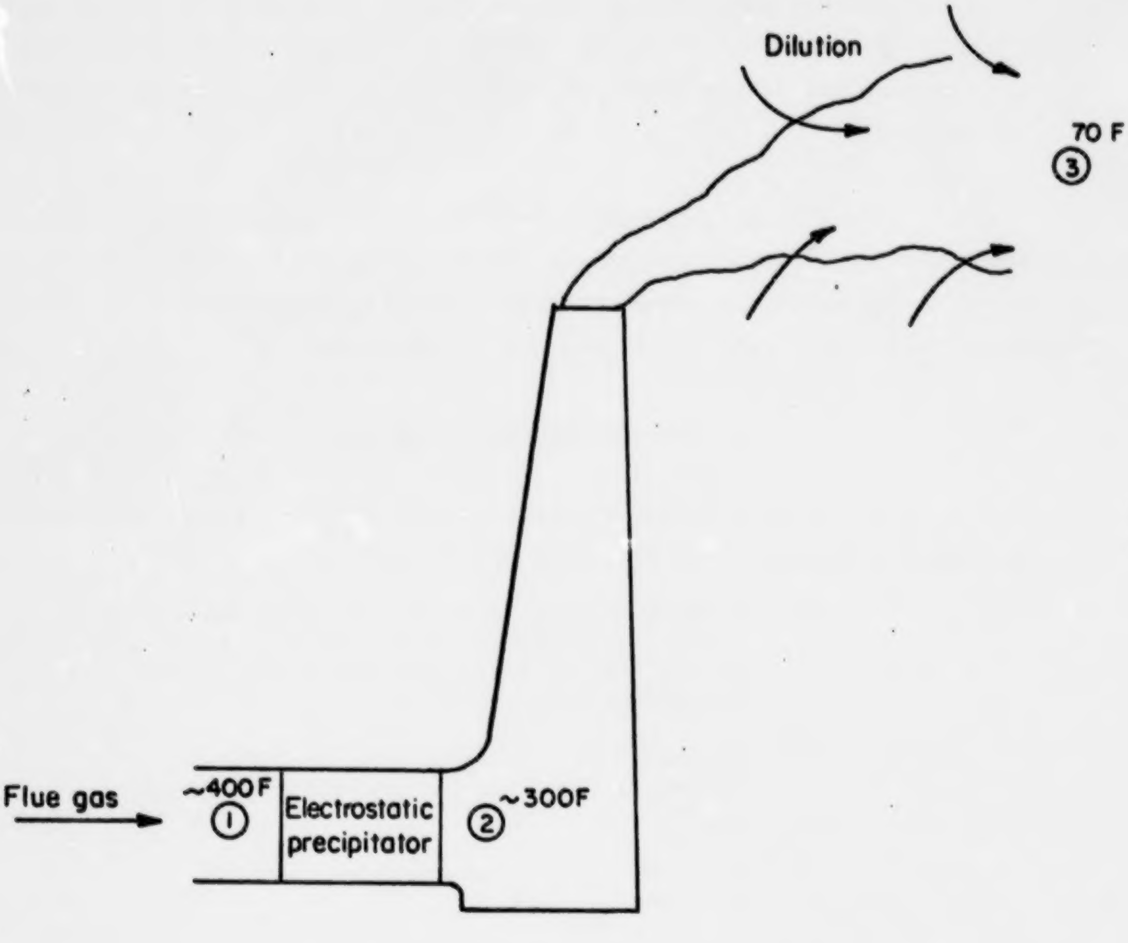
Dilution
70 F
③
Flue gas
~400 F
①
Electrostatic precipitator
②
~300F

FIGURE 1. LOCATIONS AT WHICH COLLECTED SAMPLES MAY REFLECT PARTICULATE-FORMING REACTIONS

Obviously, sampling the plume at 70 F (Point 3) is impractical, although the proposed definition of particulate (I-2) includes any condensed particles at this point.

Primary variables in the sampling train that might affect reactions of interest include filter temperature (either at gas temperature with an in-stack filter or heated to 220 F) and the presence of an impinger in the train.

The following sections consider chemical processes that may cause the formation of particulate matter and include a discussion of the state of the matter existing at various sampling points and of the reactions that might occur on filters and on impingers.

Origins of Particulate Matter

Particulate matter can be discussed in four classes according to source and sequence of information:

(A) Solid or molten particles, largely inorganic, that existed in the hot flue gases at the time of entry into the stack particulate-control equipment

(B) Nucleated material from supersaturated vapors in the gradually cooling flue gases

(C) Material added by physical or chemical sorption

(D) Condensible material that originates through further chemical reaction, whether in the stack or in the sampling train, and which adds onto or modifies the existing particulate.

(A) Inorganic Particulate, Solid or Molten Existing in the Hot Stack Gases

By the time the electrostatic precipitator is reached in the combustion flow system, most of the condensible inorganic components have already formed particulate materials. As the particulate production is judged primarily on a weight basis, further interactions of the various metal oxides with each other are of little concern so long as the particle size is in a range to permit efficient collection.

Of more concern are those compounds formed by interaction of the particulate metal oxides with the nonparticulate acidic gases present. Thus, for example, one milligram of Fe_2O_3 in the stack gases may become 2.5 mg of $Fe_2(SO_4)_3$ by reaction with sulfur oxides present in the hot gases. Possible chemical interactions are

$$Fe_2O_3 + 3SO_2 + 3/2\ O_2 \rightarrow Fe_2(SO_4)_3$$

or

$$Fe_2O_3 + 3H_2SO_4 \rightarrow Fe_2(SO_4)_3 + 3H_2O.$$

Similar reactions can be written for the other metal oxide components of the fly ash.

The actual reaction process is presumably a complex of simultaneous competitive reaction to form sulfates and water from oxides, free acid, and SO_3. The reactions and products would vary with temperature. This reaction process is well illustrated by the investigation of Jacklin, Anderson, and Thompson$^{(2)}$ into the composition of fireside deposits in oil-fired boilers.

Figure 2 shows the average deposit analysis for each of the five boiler sections studied by Jacklin, et al.$^{(3)}$ The parallel rise of Fe_2O_3 and SO_3 in the final three boiler sections is in large part due to the chemical interaction of H_2SO_4 with the iron (oxide) surfaces beginning well above 500 F. The relatively large concentration of SO_3 in all the boiler sections

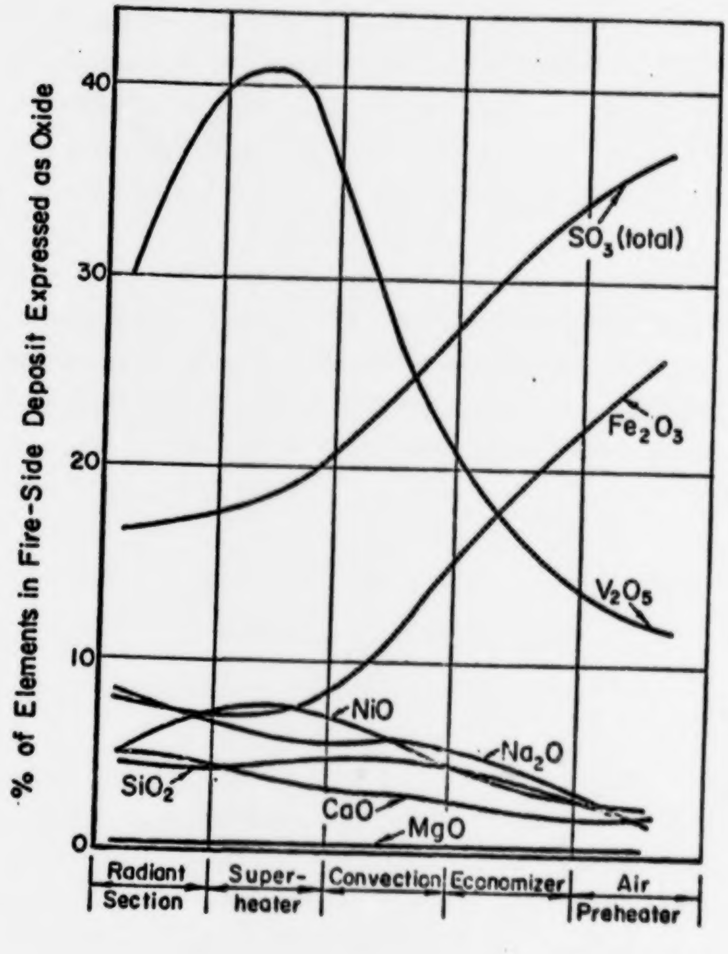

FIGURE 2. TYPICAL DISTRIBUTION OF DEPOSITS IN OIL-FIRED BOILERS(3)

indicates that the chemical retention of SO_3 is important in deposits even at temperatures well above the dew point of the aqueous H_2SO_4 mixture present in the stack gases. In such boiler systems, the bulk of the stack gases have been cooled 2000 F in a travel time of 6 sec or less, and the occurrence of supersaturation conditions for various components of the stack gases is a driving force for reactions of the sort to form particulate.

For present purposes, any process that may influence the weight of particulate by 1 percent or more is worthy of consideration. In this regard, the "Relative Importance" column of Table 1 is of interest. Thus, the column indicates that the retention in the sampling rig of only 0.1 percent of the SO_2 as sulfite would be important gravimetrically, similarly 0.002 percent of the CO_2 and 0.8 percent of the NO_x would be important if retained as acids or as salts of those acids. Thus, the reaction of extremely small quantities of these gases could contribute significantly in particulate measurements. Hence, in experiments and analyses to predict the possibilities of contribution by these acids to particulate measurements, a high level of accuracy is needed.

Sudden cooling of the gases can generate nonequilibrium conditions that can lead to formation of salts from these gases. These salts may or may not persist during sample collection, depending on conditions.

(B) Nucleated Material From Supersaturated Vapors in the Gradually Cooling Flue Gases

The formation of droplets from supersaturated vapors can be a significant source of particulates. The amount so formed depends upon the rate and mechanism of formation. The various processes are discussed here.

Following the treatment of Green and Lane,(4) the self-nucleation and growth of a droplet of condensible from a supersaturated vapor depends upon the effects of the droplet size on its vapor pressure. In the absence of an ion or dust particle to serve as the nucleus, grouping of near-neighbor molecules of condensibles can serve as nuclei. These groupings arise during the statistical fluctuations of position of the individual molecules in motion in the gas phase. The groupings formed in this way become stable droplets if the existing partial pressure, P, and the droplet radius, r, have the relationship

$$\ln \frac{P}{P_\infty} = \frac{2\gamma M}{RT\rho r} ,$$

where P_∞ is the vapor pressure of the condensible over a flat surface, γ is the surface tension, M the molecular weight, and ρ the density of the droplet material. This relationship leads to the important concept of a critical droplet size of radius r_c. All droplets with $r<r_c$ have greater vapor pressure than those of critical size and evaporate, while those with $r>r_c$ have lower volatility and grow further. Thus, formation of droplets, either by self-nucleation or by condensation on prexisting particles, requires that nuclei of the critical size or larger exist in the gas stream. As the gas stream cools P_∞ decreases rapidly and, with a given partial pressure of condensible, the critical radius becomes smaller so that more droplets are created. However, during sampling, the rate of formation of condensed material will depend on the number and size of nuclei remaining in each portion of the sampling train.

Because the amount of H_2SO_4 present is relatively large, the nucleation of aqueous H_2SO_4 droplets below the dew point is of most interest. First of all, equilibrium calculations for the reaction $SO_3(g) + H_2SO_4(g)$ indicate that essentially all SO_3 is converted by this reaction to H_2SO_4 (gas) in the flue gas at 400 F and below. The calculations for this equilibrium are given in Appendix A.

If the flue gas mixture contains 4×10^{-2} mole fraction water and 3×10^{-5} mole fraction H_2SO_4 formed by the above equilibrium reaction, total condensation of the water will yield a liquid that contains 0.075 mole percent H_2SO_4 in water. The liquid corresponds to approximately 0.04 M H_2SO_4. The work of Parkinson$^{(5)}$ indicates that this liquid also would be capable of dissolving a minor amount of SO_2. For 0.058 M H_2SO_4, which is somewhat more concentrated than the acid assumed here, the solubility at 70 F is about 3×10^{-4} lb moles SO_2/ft^3 acid. In metric terms this is 31 mg SO_2/1 of acid solution.

The dew points of aqueous H_2SO_4 vapors of the sort considered here have been determined and summarized by several investigators. Some of the following earlier data were summarized in 1963 by Miller, et al.(3) The following data for a number of earlier workers is summarized from that report.

Data published by Rendle and Wilsdon(6) on the relation of the SO_3 content of the combustion gases and of the dew point of the gases to the sulfur content of fuel oils are presented in Figure 3. Results of several other investigations also have been plotted. Consequently, the type of oil, ash content, and combustion conditions differ for the various sets of points. Although the plot of SO_3 content shows considerable scatter, it is apparent that with more than 0.5 percent sulfur in the oil, the SO_3 content of the gases does not increase in direct proportion to the increase in sulfur.

The dew-point plot brings out two important points (1) there is a rapid initial rise in dew point with the first increment of sulfur in the fuel. For an estimated dew point of 100 F with no sulfur (the water dew point), an increase to 260 F (H_2SO_4 dew point) is found with 1 percent sulfur; (2) there is a relatively small rise in dew point as the sulfur in the fuel oil increases from 1 to 6 percent. Even if an economical method of removing sulfur from oil were available, a reduction from 6 to 1 percent would lower the dew point only from 300 to 260 F. It would be necessary to achieve almost complete removal of the sulfur to obtain a significant drop in dew point.

Large changes in the water-vapor content of flue gases cause only slight changes in acid dew point. The variation of dew point with sulfuric acid content of gases having different water-vapor concentrations is shown in Figure 4, where the range from 0.5 to 15 percent water vapor changes as the dew point changes only 30 to 40 F for the medium-to-high acid contents indicated.

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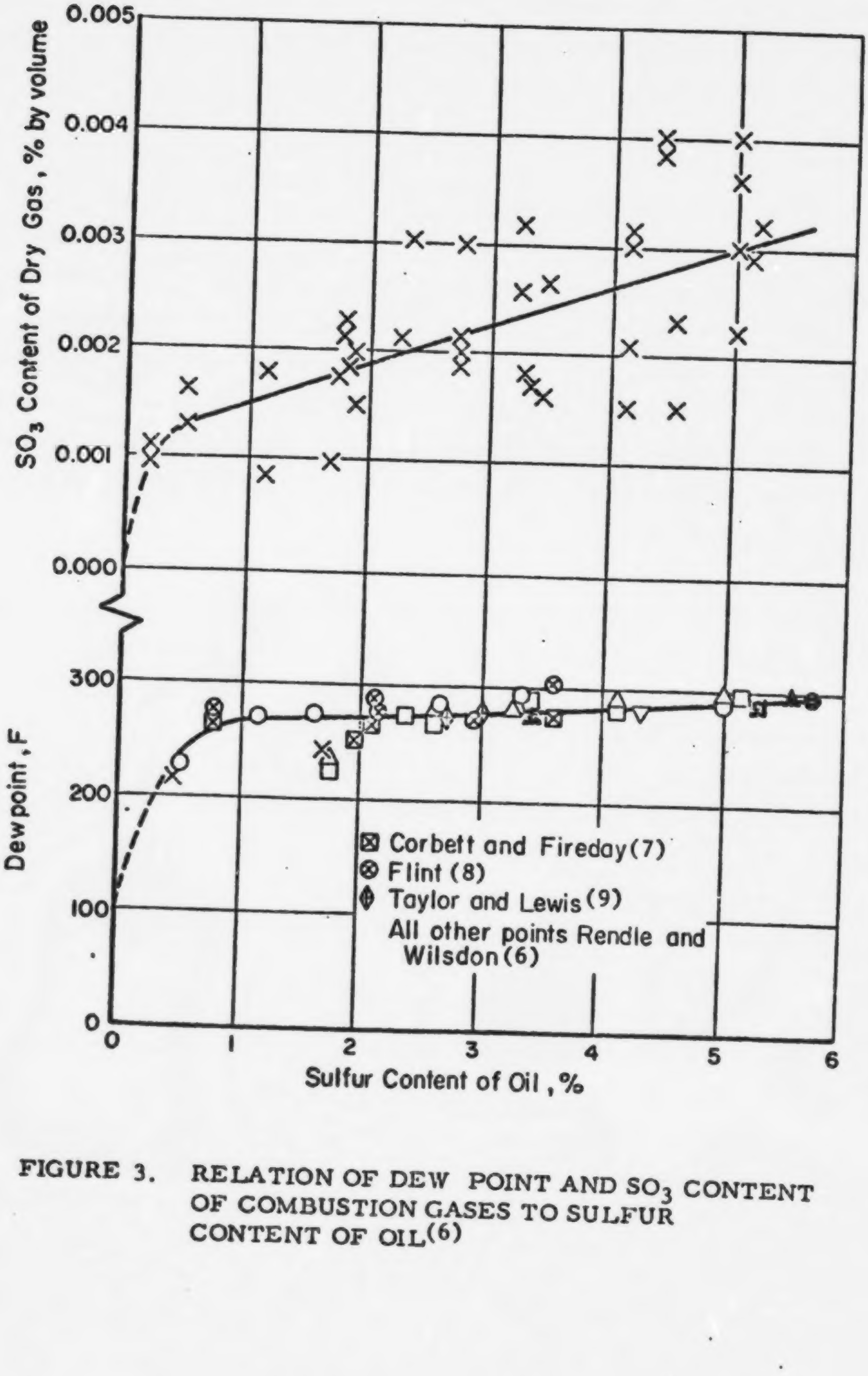


FIGURE 3. RELATION OF DEW POINT AND SO_3 CONTENT OF COMBUSTION GASES TO SULFUR CONTENT OF OIL(6)

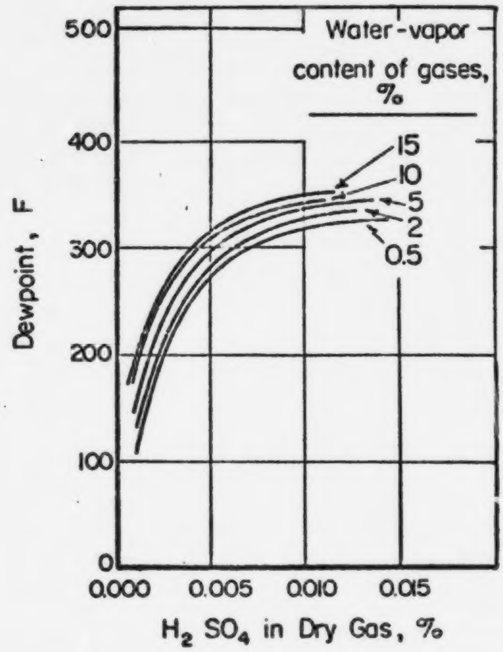


FIGURE 4. VARIATION OF DEW POINT WITH H_2SO_4 CONTENT FOR GASES HAVING DIFFERENT WATER-VAPOR CONTENTS(10)

More recently, Lisle and Sensenbaugh(11) summarized the existing data and made additional experiments to verify the dew-point data. Figure 5 is a summary of the results obtained by them using the method of Goksøyr-Ross.(1) These data are quoted and used as the bases for ASME PTC 19.10.

(C) Material Added by Physical or Chemical Adsorption

In the above considerations, only supersaturated vapors are involved. The situation becomes more complex when the processes of physical and chemical adsorption are considered. The distinction between the two is usually made by considering physical adsorption to pertain to processes with energies of adsorption less than some critical value, e.g., 10 kcal/mole, and chemical adsorption is represented by all processes with energies of adsorption greater than the critical value. Because of the lower energies

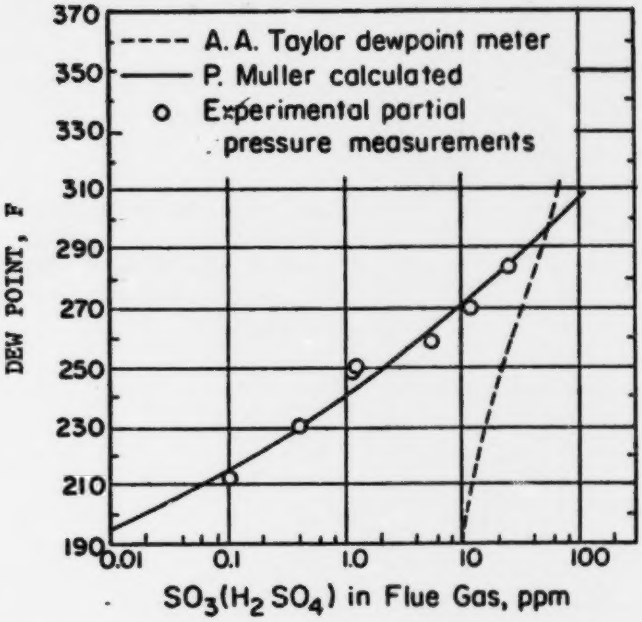


FIGURE 5. DEW POINT AS A FUNCTION OF H_2SO_4 CONCENTRATION

involved, physical adsorption is pressure dependent and may be described in terms of a pressure ratio, $P/P_s<1.0$, where P is the existing partial pressure of the vapor and P_s is the saturation vapor pressure needed to cause condensation of the vapor at the temperature concerned.

In the Brunauer, Emmett, and Teller (BET) theory of multilayer physical adsorption,(12) a model is developed based on the Langmuir adsorption isotherm in which the volume of gas, v, adsorbed by pressure, P, is related to the saturation vapor pressure of the gas, P_s by

$$\frac{P}{v(P_s-P)} = \frac{1}{v_m c} + \frac{c-1}{v_m c} \bullet \frac{P}{P_s} ,$$

where v_m is the unit volume of adsorbed gas equivalent to a single molecular layer on the adsorbing surface, and where, to a first approximation,

$$c = \exp [(q_1 - q_L) RT] ,$$

where q_1 is the heat of adsorption of the first layer and q_L is the latent heat of liquefaction of the adsorbate. Commonly, the volume of adsorbed gas approaches v_m at value of $P/P_s<1$, and depends on the value of the excess heat of adsorption for the first layer as described by the constant c. For example, in the physical adsorption of water vapor at ordinary temperatures on inert organic surfaces, we might anticipate q_1 to be 14 k cal and $q_1 - q_L \approx 4$ kcal. Adsorption of this sort leads to monolayer adsorption at about $P/P_s \approx 0.4$ at 27 C or of the order 40 percent of saturation.

Other treatments of adsorption(13) serve to model the effects of pressure at small degrees of surface coverage and indicate the P/P_s values of 10^{-5} or less may be needed to limit adsorption to about 1 percent of the available surface. This persistence of adsorption at low fractions of saturation pressure can result in considerable error in the estimation of condensible components of the stack gases if the possibilities for retention of such materials at the filter are not considered during the processing and particularly the drying of samples.

Chemical Adsorption. The process of chemical adsorption is conveniently approached through use of a model, described by Hobson(13) for the effect of partial pressure and adsorption energy on the extent of adsorption. Thus, in Figure 6, the fractional coverage of the surface, θ, is described in terms of a Langmuir model of uniform surface for which the desorption energy, E, for the adsorbed material is constant. The parameter K is a function of temperature, T (K) and molecular weight, M, of the adsorbing gas and, following Hobson, is equal to $K = 1.76 \times 10^4 (MT)^{1/2}$. The dotted lines in Figure 6 show how the surface coverage for a gas of molecular weight 28 (N_2) would be expected to vary as a function of partial pressure and energy of surface interaction (E/RT). The higher values of E/RT, e.g., ≥ 16, correspond to our definition of chemical-adsorption processes at room temperature and the range of E/RT shown covers the full range of adsorption processes including the transition betwen physical and chemical adsorption.

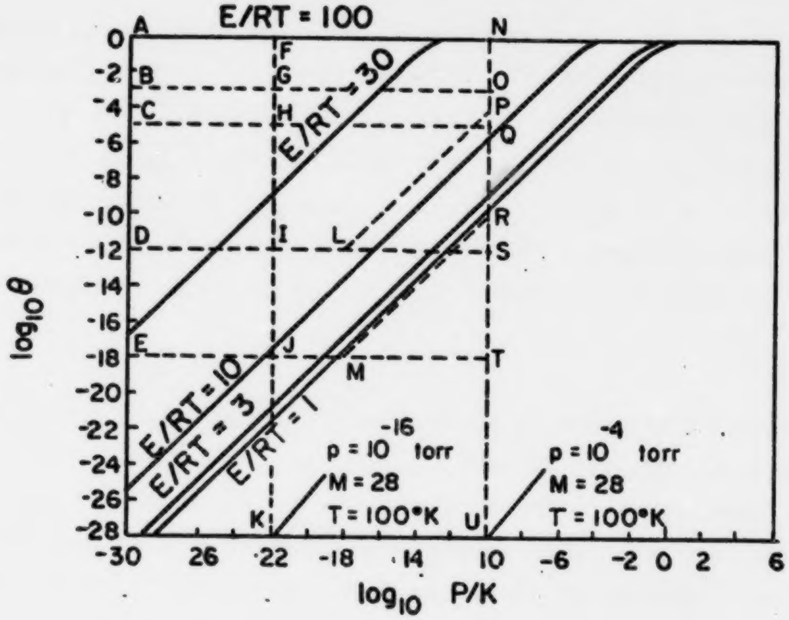


FIGURE 6. LOG$_{10}$ θ VERSUS LOG$_{10}$ P/K FOR SIMPLE LANGMUIR MODEL

Inspection of some available adsorption data indicate that the heats of adsorption of SO_2, H_2SO_4, and such vapors on oxides, such as fly ash, may be anticipated to fall generally in the interval 5 to 15 kcal. In that event, the BET model shows that monolayer coverage of all surfaces by these vapors at room temperature occurs at vapor concentrations equal to a few tenths of saturation. Similarly, from Hobson, fractional coverage of a few percent of the surfaces by adsorbed vapors occurs at P/K of the order of 10^{-8}, or vapor concentrations of a few parts per million at 1 atmosphere. These two estimates establish the limiting concentrations of each gas-mixture component that can participate in appreciable adsorption at the temperature chosen. At higher temperatures the pressures required would be somewhat higher, but the implication of high surface coverages at vapor pressures well below saturation remains valid. Two questions are of interest:

(1) Assuming complete monolayer adsorption on all particulate and filter surfaces, how much is the apparent weight of particulate altered?

(2) As the adsorbed layer will determine the chemical reactivity of the particulate emitted, what can be said about the probable nature of that adsorbed layer?

The surface area of the particulate can be estimated from

$$S = \frac{6}{\rho d}\,, \quad \text{where}$$

S = surface area, m^2/g
ρ = density g/cc
d = particle diameter, micrometers, μ

so that, for a material of density = 2.0, the particulate before the precipitator would have surface of $\frac{6}{2\ (10)} = \frac{6}{20} = 0.30\ m^2/g$.

For the performance assumed in Table 1, the effect of the precipitator on particulate surface area remaining in the stack gas is illustrated by the following:

		Surface Area	
		m^2/g	m^2/m^3
particulate before precipitator, 10μ, 9.16 g/m^3	=	0.30	2.74
particulate after precipitator, 0.5μ, 0.458 g/m^3	=	6.0	2.74 .

Note that although the precipitator removed 95 percent of the mass and reduced the particle size twenty-fold, essentially none of the particulate surface was removed. As the chemical importance of the particulate is apt to be related to the amount of reactive surface present, this may be an important observation. The 2.74 m^2 of surface/m^3 stack gas can adsorb approximately $2.74 \times 1 \times 10^{-5}$ moles of vapor of low molecular weight, e.g., H_2O. This would be $2.74 \times 10^{-5} \times 18 = 49.5 \times 10^{-5}$, or approximately $5 \times 10^{-4}\ g/m^3$ gas. As the particulate weight is 0.458 g/m^3, the adsorption is negligible on a weight basis, even if monolayer amounts of each vapor were retained.

However, the adsorption capacity of 2.74×10^{-5} moles/m^3 gas is sufficient to retain a substantial fraction of the trace organic materials that may be present. For this reason, high-surface-area portion of the sampling train, e.g., the particulate and the filter medium, must be examined for such ingredients. Thus for BaP at 25 μg/1000m , a partial pressure of $P/P_s \sim 10^{-8}$ might easily produce surface coverage of 0.1 percent. This would amount to 10^{-8} moles per m^3 gas compared to the 10^{-10} moles/m^3 actually found in the gas. Thus, far more of BaP or similar ingredients may be retained by adsorption on the filter than would be found in the effluent gases.

In considering the chemical nature of the adsorbed films that can form in this way, it is important that the simultaneous physical adsorption of two or more components of the gas mixture at a surface be favorable to chemical reaction between the adsorbed components. Thus, possibilities exist for chemical change in stack gases during sampling. The considerations presented here indicate that high concentrations of minor flue-gas components may exist on particle surfaces. Surface influences may be recognizable experimentally by using widely different temperature conditions at the point where the solid particulates are expected to be collected, or by doping the stack gases to alter ambient concentrations of individual components.

(D) Condensible Material That Originates Through Further Chemical Reaction, Either in the Stack or in the Sampling Train

Several reactions by which SO_2 might react to form condensible material, either in the stack or in the sampling train, include

Reaction 1. SO_2 oxidizing to SO_3 at stack temperatures in contact with fly ash having catalytic properties

Reaction 2. SO_2 oxidizing and being retained as SO_4^{-2} on surfaces of oxide particulate

Reaction 3. SO_2 absorbing on a liquid-phase water droplet or in the impinger solution, and oxidizing by reaction with dissolved O_2.

Considering Reaction 1, the oxidation of SO_2 to SO_3 in the presence of O_2 is rapid on V_2O_5 or Pt surfaces at about 900 F, and most kinetic treatments are complicated by the need to consider the diffusion transport limitations in the pores of the catalyst. Two approaches have been used to estimate the rate of oxidation at stack temperature. To maximize the estimate of the extent of reaction, the particulate may be imagined to be retained for 1 hour on a filter in the stack gas. In addition, the following assumptions may be made

- There are no diffusion limitations
- The fly ash is as good a catalyst as the commercial material but the filter (or fly ash) is exposed to the reactant gases at 400 F instead of the usual temperature range for catalytic oxidation of SO_2.

The two treatments used for the rate of oxidation of SO_2 to SO_3 in the region of kinetic control are:
According to Calderbank(14)

$$r\left(\frac{\text{moles } SO_2 \text{ converted}}{\text{g catalyst-sec}}\right) = \exp\left(\frac{-31,000}{RT} + 12.07\right) \cdot \frac{P_{O_2} \cdot P_{SO_2}}{P_{SO_2}{}^{1/2}}$$

$$= \exp\left(\frac{-53,600}{RT} + 22.75\right) \quad \frac{P_{SO_3} \cdot P_{O_2}{}^{1/2}}{P_{SO_2}{}^{1/2}} ,$$

where P is in atmospheres and T = °K.

According to Kodles, et al.(15)

$$r\left(\frac{\text{moles}}{\text{g cat-hr}}\right) = 6.04 \times 10^9 \quad \exp\left(\frac{-32,414}{RT}\right) \qquad \left(N_{SO_2} \cdot N_{O_2}{}^{1/2} - \frac{N_{SO_3}}{K}\right),$$

where T is °K, N's are mole fractions, and K = equilibrium constant for the conversion of SO_2 to SO_3 at temperature, T. For this evaluation a maximum rate was calculated with the Kodles equation by putting $N_{SO_3} = 0$.

Both estimates show 10^{-8} g SO_2 or less oxidized to SO_3 in the given mixture in 1 hour time per m^3 of gas flowing. If the filter was exposed to gas at 1 cu ft/min, then about 1.7 m^3 gas would be exposed to the filter in 1 hour. Thus, the total SO_2 oxidized, $<2 \times 10^{-8}$ g, is negligible compared to either 0.45 g of the fly ash or the SO_3 already present. The high-temperature catalysts used for commercial oxidation of SO_2 do not retain sufficient activity at stack temperature to be capable of appreciable oxidation of the SO_2 in the assumed gas mixture. Therefore, the quantity of condensible formed by this reaction should not be significant in the presence of fly ash.

A qualitative approach to Reaction 2 can be made through the published data for the DAP-Mn process$^{(16)}$ in which manganese oxide is used as an absorbent which, in the presence of O_2 forms manganese sulfate. Thus,

$$MnO_x \cdot iH_2O + SO_2 + \frac{1}{2}(2-x)O_2 \rightarrow MnSO_4 + iH_2O.$$

In this process, x is about 1.5 to 1.8 and i is 0.1 to 1.0. The oxide has been found to have a high affinity for SO_2 in the temperature range 100 - 180 C (i.e., 212 to 356 F). In that range, at least, the effect of temperature on the rate of absorption process is negligible. The authors find that the results can be expressed by $\ln (Yo/Y) = kmx^n \cdot t$, where

Yo = concentration of SO_2 in inlet gas, vol. percent
Y = concentration of SO_2 in outlet gas, vol. percent
m = concentration of absorbent, $gMnO_x/m^3$ gas
t = residence time of gas, sec

and then suggest suitable values of n and k are -1.5×10^{-4}, respectively. On this basis, assuming that particulate is all as active as this MnO_x and using the estimate (see Table 1) that a 0.1 percent retention of SO_2 would be important,

$$\ln \frac{1000}{999} = 1.5 \times 10^{-4} \ (1.8)^{-1.5} \quad (0.458)\ t$$

$$0.001 = 0.31 \times 10^{-4}\ t$$

$$t = 30 \text{ sec.}$$

Hence, the adsorption of SO_2 and fixation as sulfate is conceivably important in the filter section of the sampling rig, if much of the particle surface is as active as MnOx.

The contribution of Reaction 3 (the absorption of SO_2 in a water phase followed by oxidation by dissolved O_2 to form sulfate) is difficult to estimate because of the influence of pH on the reactions. Data obtained under the conditions usually used for investigation of SO_2 absorption would differ greatly from those of the impinger. Futhermore, because the reaction proceeds by a chain mechanism involving radical formation processes in the water phase, many materials can serve either to accelerate or retard the reaction. In general, the rate of sulfite oxidation in solution is described by(14)

$$\frac{d\,S_t}{dt} = \frac{g\,[HSO_3^-]}{[H+]^{1/2}} \quad ,$$

where S_t represents the total concentration of sulfite species and g is a rate constant that includes contributions by various free radical processes and is dependent on the dissolved O_2 concentration. In the impinger, the constant supply of dissolved SO_2 from the flowing gases and the effect of dissolved acids generate conditions radically different from those used experimentally in the investigation of sulfite oxidation. First-order rate constants for the oxidation by dissolved oxygen from normal air(17) show half-times for reaction of about 200 seconds at 35 C for well-stirred sulfite solutions in neutral and mildly alkaline solution. In these experiments variations in initial pH in the range 6.95 to 8.20 seems to affect the degree of oxidation (in the absence of replacement SO_2 of HSO_3^-) but not the initial rate.

Conclusions Pertaining to Particulate Formation and Reactions in Flue Gases

Our conclusions are stated by considering the several stages of the flue-gas handling system as analogous to sampling stations from which particulate is sampled and characterized. These stations are

Station 1:	In-stack filter ahead of the electrostatic precipitator (at Sampling Point 1 in Figure 1)
Station 2:	In-stack filter after the electrostatic precipitator (at Sampling Point 2 in Figure 1)
Station 3:	External filter maintained at a temperature of 220 F
Station 4:	Diluted plume at 70 F or (theoretically the impinger).

In practice, these stations are not a true sequence. For example, a particulate sampling train normally would include a filter at the conditions of either Station 1, 2, or 3, and may or may not include an impinger (Station 4). However, for the purpose of this discussion, the conditions at each station are presented as consecutive and in the order of decreasing temperature.

Station 1: In-Stack Filter Ahead of Electrostatic Precipitator

At this station, the ash components have essentially all condensed to form solid particulate. Water vapor has begun to adsorb on all surfaces including that of the particulate, but the monolayer is quite incomplete because of the high stack temperatures. The SO_3 in the stream will be 98.7 percent converted to H_2SO_4 at this station and the relatively low concentration of H_2SO_4 formed in this way would be physically adsorbed competetively with the more concentrated H_2O vapor. Chemical reaction of H_2SO_4

with the particulate will contribute further to H_2SO_4 retention so that the particle surface may hold a relatively strong concentration of sulfate or aqueous H_2SO_4. The particulate provides an estimated 2.8m^2 surface/m^3 gas and the adsorbed monolayer on this surface will be negligible in mass compared to the mass of the particles themselves. As shown earlier, the particulate collected on an in-stack filter at this point, if retained there for 1 hour with 1 cu ft/min flow, would generate a negligible amount of SO_3 from SO_2 in this sample gas stream, even if the particulate surface equalled the catalytic action of commercial high-temperature catalytic oxides. The rapid cooling of hot gases prior to this station may have generated other salts such as the alkaline earth carbonates, which will tend to be decomposed as the sulfuric acid accumulates. The degree of this conversion is unknown.

Station 2: In-Stack Filter After the Electrostatic Precipitator

At this point, H_2O adsorption is extensive and a major part of the surfaces is now covered by adsorbed vapor. The conversion of SO_3 to H_2SO_4 is essentially complete at this temperature (about 350 F) and relatively high concentrations may be expected in the adsorbed layers. The precipitator has removed 95 percent of the particulate mass and reduced the average size from 10 μ to 0.5 μ, but nearly all of the initial surface area remains. Nevertheless the mass of the adsorbed layer is still negligible. Available data(16) confirm the expectation that the irreversible SO_2 absorption and then oxidation to sulfate by processes such as

$$(1)\quad MO_x \cdot iH_2O + SO_2 + \frac{1}{2}(2-X)\ O_2 \rightarrow MSO_4 + iH_2O$$

must be considered for material retained on filters at these temperatures. The particulate remaining which leaves the precipitator will serve as a nuclei for the onset of condensation of the aqueous H_2SO_4 to form droplets of diameter greater than a critical diameter defined by the degree of supersaturation of vapor.

Station 3: External Filter at 220 F

At this station, the temperature has fallen to the point where most of the H_2SO_4 has condensed to form aqueous liquid, if it has not already been absorbed by the metal oxide particulate material. Dilution of the flue gases with air would lower the H_2SO_4 dew point somewhat, but the equilibrium vapor concentration of H_2SO_4 at this temperature, 0.1 ppm, assures that at least 90 percent of the H_2SO_4 would be expected to condense even at 20:1 dilution ratio. The chances that some SO_2 may be oxidized and retained as sulfate on the filter catch cannot be disregarded. For the cases of CO_2 and NO_x, significant formation of salts from these gases by nonequilibrium reactions of the metal oxide particulate with the humid gases appears possible.

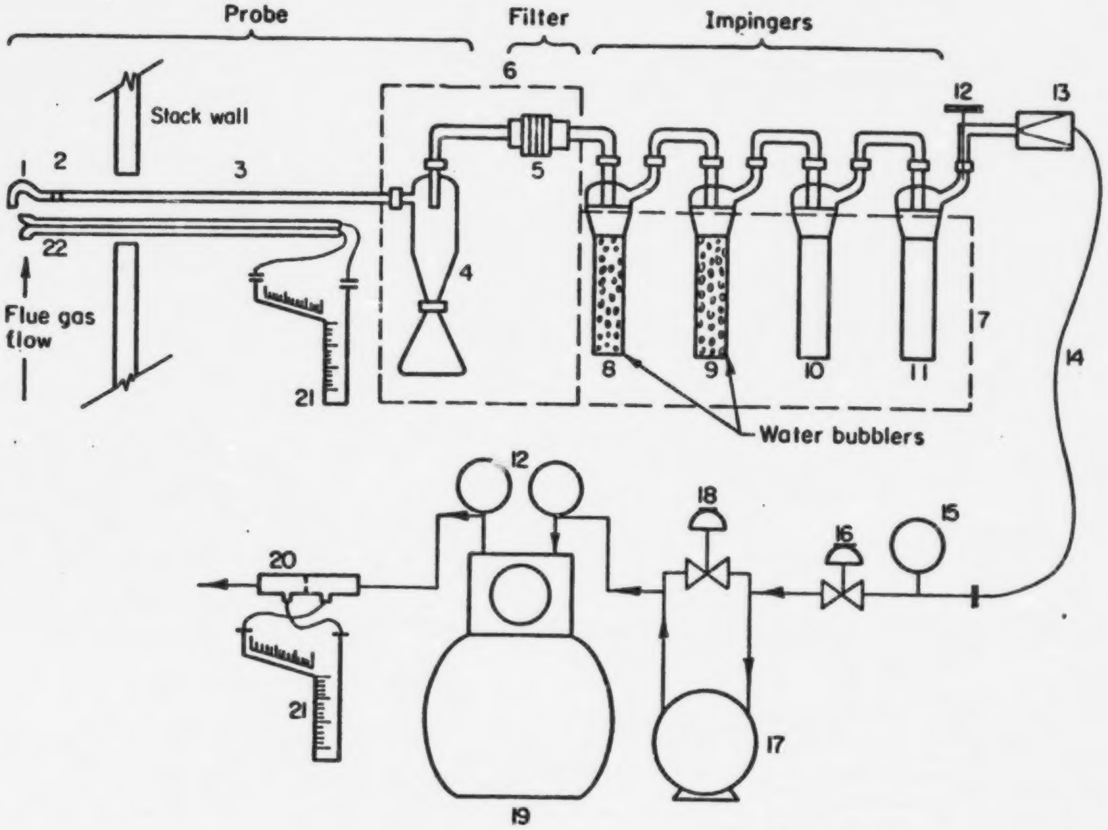
Station 4: Plume or Impinger

The degree to which SO_2, CO_2, and NO_x contribute to the condensible particulate in the diluted stack gases (plume) is not available by direct measurement. Calculations indicate that some contributions may occur in an impinger in a sampling train, but the comparison of the contributions under plume and sampling conditions remains a difficult problem for experimental investigation that has not been attempted in this program.

Sampling Train

Figure 7 shows the sampling train as used by EPA. As originally conceived, its objective was to collect dry solid particulates in the cyclone and filter and to cool the gases prior to the pump and meter section. Aside from their ability to collect "condensibles", the impingers also serve as a "backup" for the filter in case it fails from defect or faulty installation in the holder, to collect the water from the gases for measurement and to cool the gases prior to the pump and meter section.

This is the basic sampling train arrangement used for particulate sampling in this work except for research variations as noted in the Experimental Equipment and Methods section.


Probe
Filter
Impingers
6
12
13
Stack wall
1
2
3
5
4
22
Flue gas flow
21
7
8
9
10
11
14
Water bubblers
12
18
15
16
20
21
17
19

1. Stainless steel, buttonhook-type probe tip
2. Stainless steel coupling
3. Probe body, 5/8-inch OD, medium-wall Pyrex tube logarithmically wound with 25 feet 26 ga. nickel-chromium wire
4. Cyclone and flask
5. Fritted-glass filter holder
6. Electrically heated enclosed box
7. Ice bath containing four impingers connected in series
8. The Greenburg-Smith type impinger with tip removal
9. Second impinger with tip
10. Third impinger with tip removed
11. Fourth impinger with tip removed and containing approximately 175 grams of accurately weighed dry silica gel
12. Pressure gauge
13. Check valve
14. Flexible-rubber vacuum tubing
15. Vacuum gauge
16. Needle valve
17. Leakless vacuum pump
18. By-pass valve
19. Dry-gas meter
20. Calibrated orifice
21. Draft gauge
22. S-type pitot tube

FIGURE 7. EPA PARTICULATE SAMPLING TRAIN

III. EXPERIMENTAL PROGRAM

- RESEARCH PLAN
  - Phase I. State-of-the-Art Report
  - Phase II. Plan Research Program
  - Phase III. Execute the Test Program
  - Experimental Equipment and Methods
    - Multifuel Furnace Facility
      - Design Features
      - The Multifuel Furnace
      - Simulated Boiler/Economizer Section
      - Electrostatic Precipitator
      - Stack
      - Operational Characteristics
      - Analytical Methods
    - C, H, N Analyses
    - Wet Chemical Analysis for S
    - Goksøyr-Ross Procedure for SO_3 and SO_2
  - Experimental Details and Results
    - Initial Trials
    - Experimentation Using Multifuel Furnace
      - Coal-Fired Operation
      - Field Experiments
        - Effect of Drying Conditions
        - Experiments at Edgewater Power Station

III. EXPERIMENTAL PROGRAM

RESEARCH PLAN

Battelle's experimental approach to this study consists of a three-phase program:

Phase I. State-of-the-Art Review

A state-of-the-art report has identified the present knowledge of emissions from fossil-fuel combustion processes and particulate emission measurement methods.

Phase II. Plan and Prepare a Test Program

An experimental plan for the experimental aspects of the project, including the field program was reviewed by EPA. This field program was designed to provide data on emission measurements as influenced by sampling-train construction, flue-gas parameters, and the presence of particulate emission control devices.

Because of the desirability of holding combustion conditions steady during sampling, a Battelle-owned Multifuel Furnace Facility was used for most of the investigation. It is capable of firing fuel oils and coal at low rates and of generating flue gas reasonably typical of that produced in power plants. Samples from this facility can be obtained at lower cost and greater convenience than can samples from power plants. Hence, the early stages of this investigation were conducted using this furnace. The collection of samples from power plants was better defined and planned because of lessons learned in preliminary runs with the furnace at Battelle. Also, these runs produced useful data in planning details of the field work.

Unfortunately, accepted absolute or referee methods for such sampling do not exist. The method used has been to investigate the causes for changes in particulate catch that were produced by changes in sampling mode and sample-handling procedures. This experimental method has required the collection of data from pairs of experiments planned to demonstrate the effects of individual changes in experimental procedures. Such comparisons were made using single-point sampling procedures (as opposed to traverses) to reduce variables and sample-collection time.

Phase III. Execute the Test Program

The iterative procedure for investigation of sampling methods is summarized in Table A on page I-5.

a. Initial Trials Using the Laboratory Furnace

A series of samples was collected while several No. 6 residual fuel oils were fired in the laboratory furnace. Of primary concern in these trials were probe and filter materials and the importance of filter temperature.

b. Experimentation Using the Multifuel Furnace Facility

As a result of the above trials and a study of potential reactions that might occur in the sampling system as discussed in the Background Section of this report, a new series of trials was designed. These trials were intended to determine how sampling-train variables affected the collection of sulfur oxides within the train. The sampling train for these trials was basically the EPA train with modifications for specific trials. These trials utilized the laboratory furnace but with coal-firing operation.

A second series of trials was conducted using the laboratory furnace to further identify problems arising from SO_2 retention and oxidation during sampling and sample handling. For these trials, the sulfur oxide catch in the various particulate sampling rigs was compared with the sulfur oxide content of the stack gas as measured by an independent method. The Goksøyr-Ross method (G/R) was chosen for this purpose. In planning these trials, variations in both sampling and sample-handling procedures were used in the hope that it might be possible to distinguish among the several ways that SO_2 oxidation can occur. For example, the sulfate collected with the particulate was expected to represent the sum of

(1) SO_3 present in the stack gas
(2) SO_3 generated during sampling (here 40 minutes)
(3) SO_3 generated in the impinger solutions during storage under air in bottles, and transported to the laboratory (usually days or weeks)
(4) SO_3 generated during sample evaporation and analysis.

c. Field Experiments

The experience gained in the experimentation with the Battelle Multifuel Furnace was used to design a series of trials that were conducted at the coal-fired Edgewater Power Station, Lorain, Ohio, and which incorporated the most useful variations that had been tried in the laboratory. The experimentation was divided into two subseries: one intended to provide as much detail as possible regarding the amount and oxidation state of the sulfur oxides retained in the various portions of experimental sampling apparatus, and the other intended to provide a comparison of the amount and chemical composition of the particulate collected from the inlet and exhaust streams of the electrostatic precipitator.

Experimental Equipment and Methods

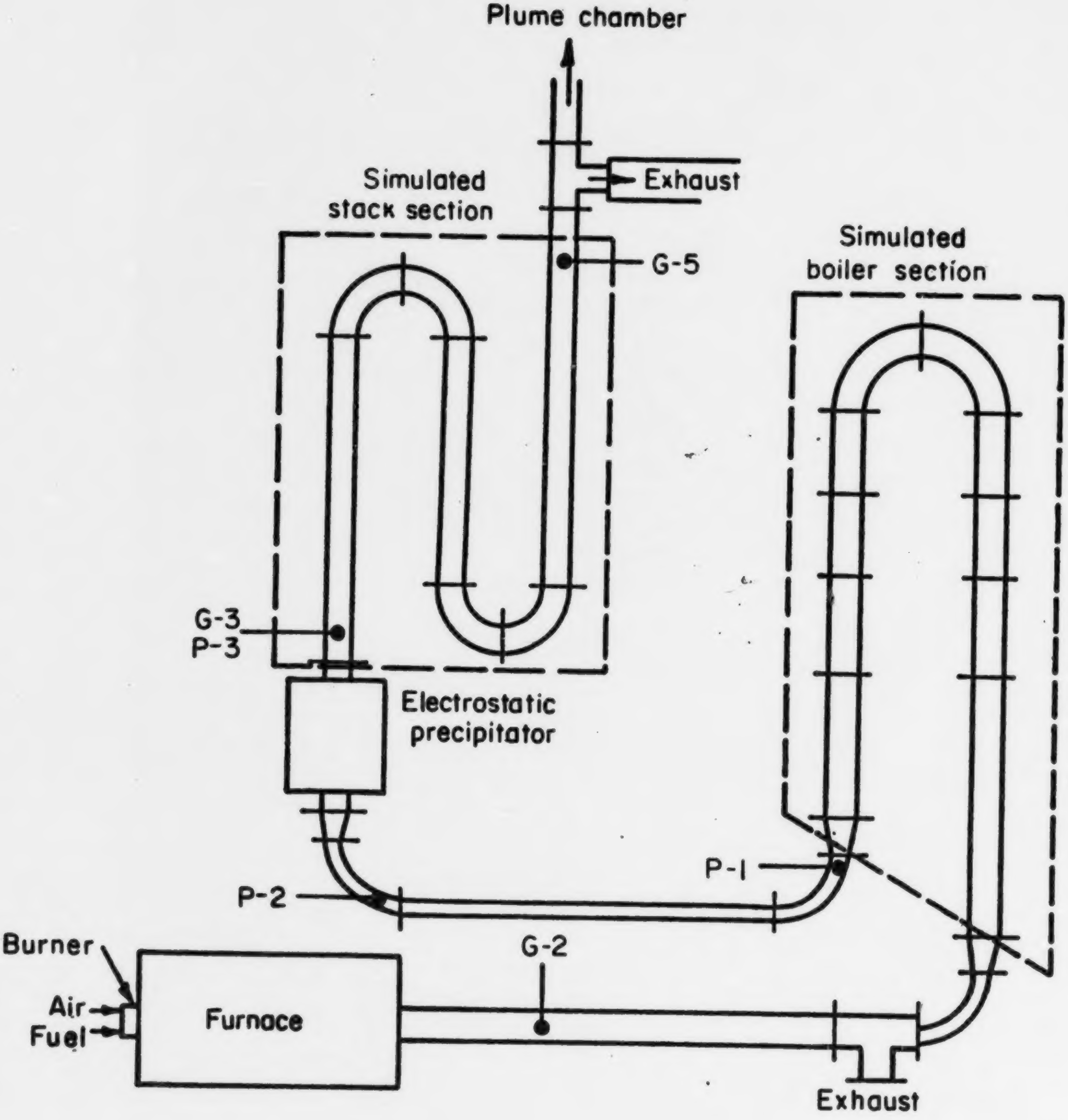
Multifuel Furnace Facility

Design Features. The multifuel furnace used for this program was designed to generate flue gas and fly ash under conditions closely simulating those of a power-generation station. This implies combustion at a high enough temperature with a proper cooling schedule to produce flue gas and fly ash having physicochemical properties similar to those of a typical central-station boiler and its associated stack and plume. In addition, the laboratory-scale system used in this program was flexible enough to permit firing with either pulverized coal or residual oil.

The Multifuel Furnace Facility was operated with an electrostatic precipitator in firing coals but without an electrostatic precipitator in firing oils. The time-temperature profiles in the other sections of the facility were appropriately adjusted for the inclusion or exclusion of the precipitator.

Figure 8 is a schematic representation of the gas combustion and flue gas conditioning system with major sections and sampling points indicated. The major sections of the system are discussed below.

The Multifuel Furnace. Figure 9 is a photograph of the Battelle Multifuel Furnace which was used on this program. This small-scale furnace consists of a cylindrical combustion chamber approximately 15 in. in diameter by 80 in. in length. The furnace is lined with three layers of firebrick and insulation to accommodate surface temperatures up to 2900 F. At the outlet, the diameter of the furnace is reduced to 5 in. to enclose the flame, provide for normal recirculation, limit radiation losses, and provide sufficient gas velocity to keep fly ash suspended in the gas stream. Viewports along the axial dimension of the furnace provide for visual access during periods of adjustment of firing conditions.


Plume chamber
Exhaust
Simulated stack section
G-5
Simulated boiler section
G-3
P-3
Electrostatic precipitator
P-1
P-2
Burner
G-2
Air
Fuel
Furnace
Exhaust

G = Gas sampling port
P = Particulate sampling port

FIGURE 8. SCHEMATIC REPRESENTATION OF MULTIFUEL FURNACE SYSTEM

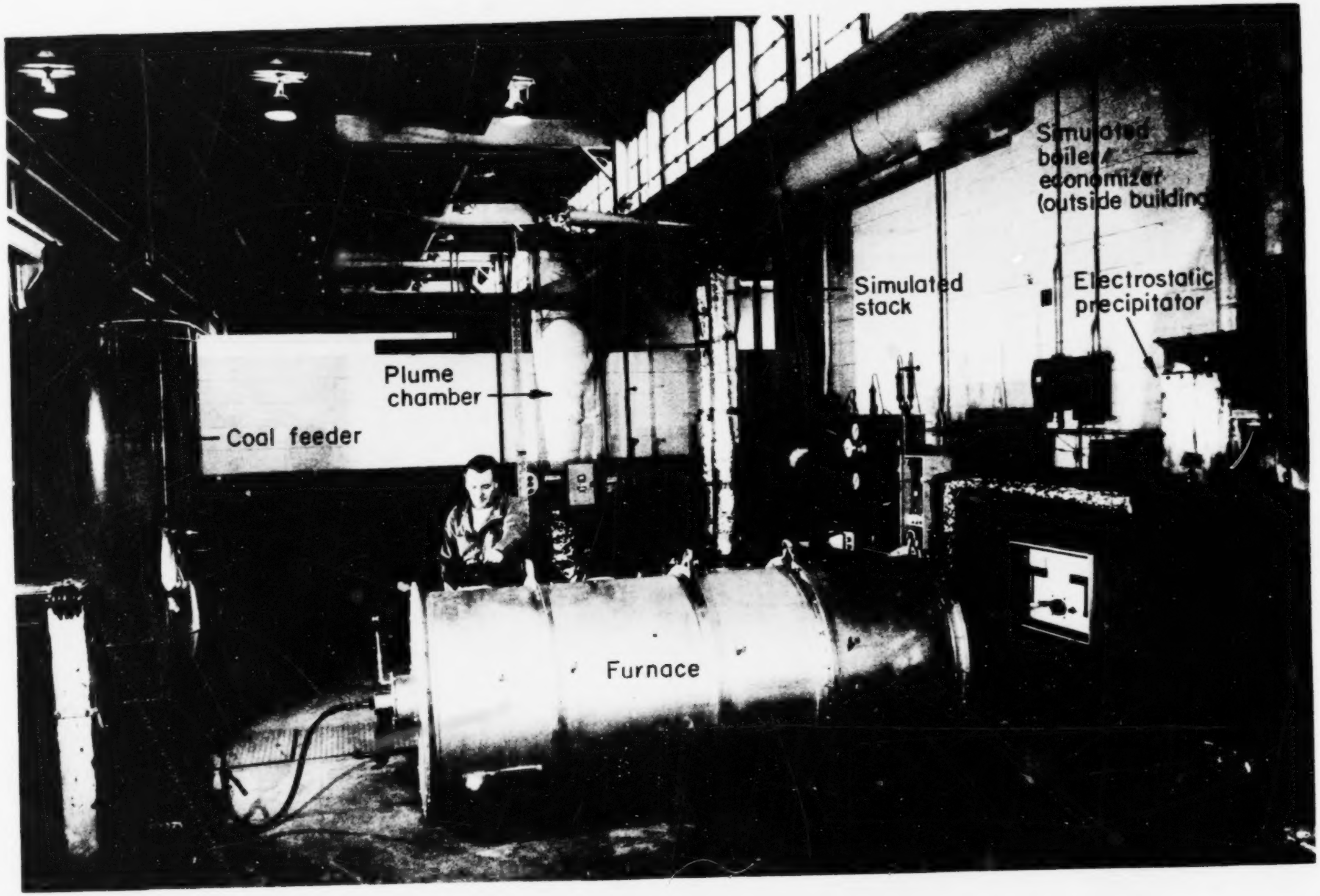

Coal feeder
Plume chamber
Furnace
Simulated stack
Simulated boiler/economizer (outside building
Electrostatic precipitator

FIGURE 9. BATTELLE MULTIFUEL FURNACE

In normal operation of the furnace, natural-gas firing was used to maintain system temperatures at approximately the desired levels on a more or less continuous basis while runs were not being made. Upon switching to either coal or oil firing, the entire system was allowed to re-equilibrate for several hours before any data were taken.

An adjustable-flow positive-displacement pump which was precalibrated was used to regulate the supply of residual oil to the furnace at about 3 gal/hr, and preheating of the oil was provided to insure the desired viscosity at the burner nozzle. With coal firing, a dispersion of the fuel in air was fed to the burner (at a rate of about 30 lb/hr) via a screw feeder mounted within a pressurized coal hopper.

Simulated Boiler/Economizer Section. The simulated boiler/economizer section of the rig was constructed of stainless steel pipe lined with a castable refractory material. Gas velocities within this section were modulated using a variable exhaust duct at the head of the section. This operation also helped in maintaining desired temperatures, and additional control over temperature profiles was gained through the use of removable insulation on the outside of the section. Gas velocities in horizontal portions of this section were typically 60 ft/sec, and velocities in vertical portions were about 5 ft/sec. Temperatures dropped from about 2600 F at the inlet to about 400 F or less at the outlet.

Electrostatic Precipitator. An electrostatic precipitator made by Precipitair was used for removal of fly ash between the boiler and stack sections of the system for runs made with coal firing. Typically, the inlet and outlet temperatures of the precipitator were 375 F and 300 F, respectively.

Stack. The 37-ft-long simulated stack section of the rig was constructed of 5 in. OD stainless steel pipe. Temperatures in the stack section could be controlled through the use of heating tape and insulation applied throughout the length of the section. For runs with residual oils, the stack temperature was maintained at about 300 F. With coal firing of the unit, the stack temperature was maintained at 250-275 F. These values are typical of central-power-station operation with these fuels. Sampling points are available at regular intervals along the stack section.

Operational Characteristics

The operational characteristics of prime interest to this program concerned the time-temperature profiles obtained in the system. Typical time-temperature profiles for oil and coal firing are shown in Figures 10 and 11. Residence times with coal firing were similar to those with oil firing except for the extra 5-sec residence time in the precipitator. Temperatures in the system were also similar for both types of fuel except for the slightly lower stack temperatures which are more typical of coal-fired power plants.

Analytical Methods

Figures 12 through 15 shows the methods of analysis used as described in the following paragraphs. Experimental variations in sample handling and in preparation for analyses are discussed in the section on the Experimental Details and Results for each series of trials. Because the research work was planned as an iterative program, each series of trials employed techniques that drawn from the experience in the previous series. For this reason the arrangements for each series of trials and the results obtained from each are described together. The Discussion section describes the overall relations and meanings that have been drawn and which serve as the basis for the Conclusion section.

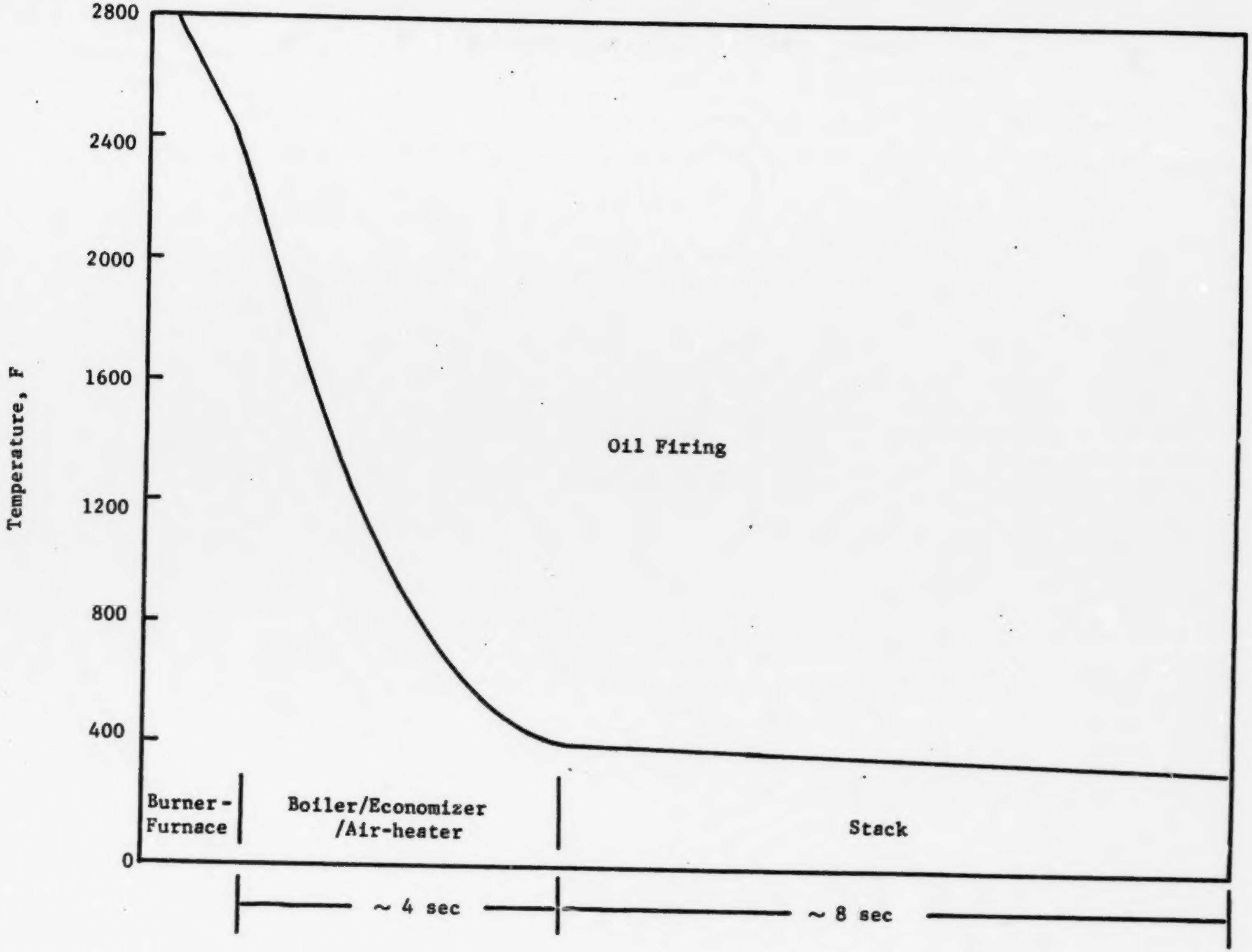


FIGURE 10. TIME-TEMPERATURE PROFILE TYPICAL OF OIL FIRING

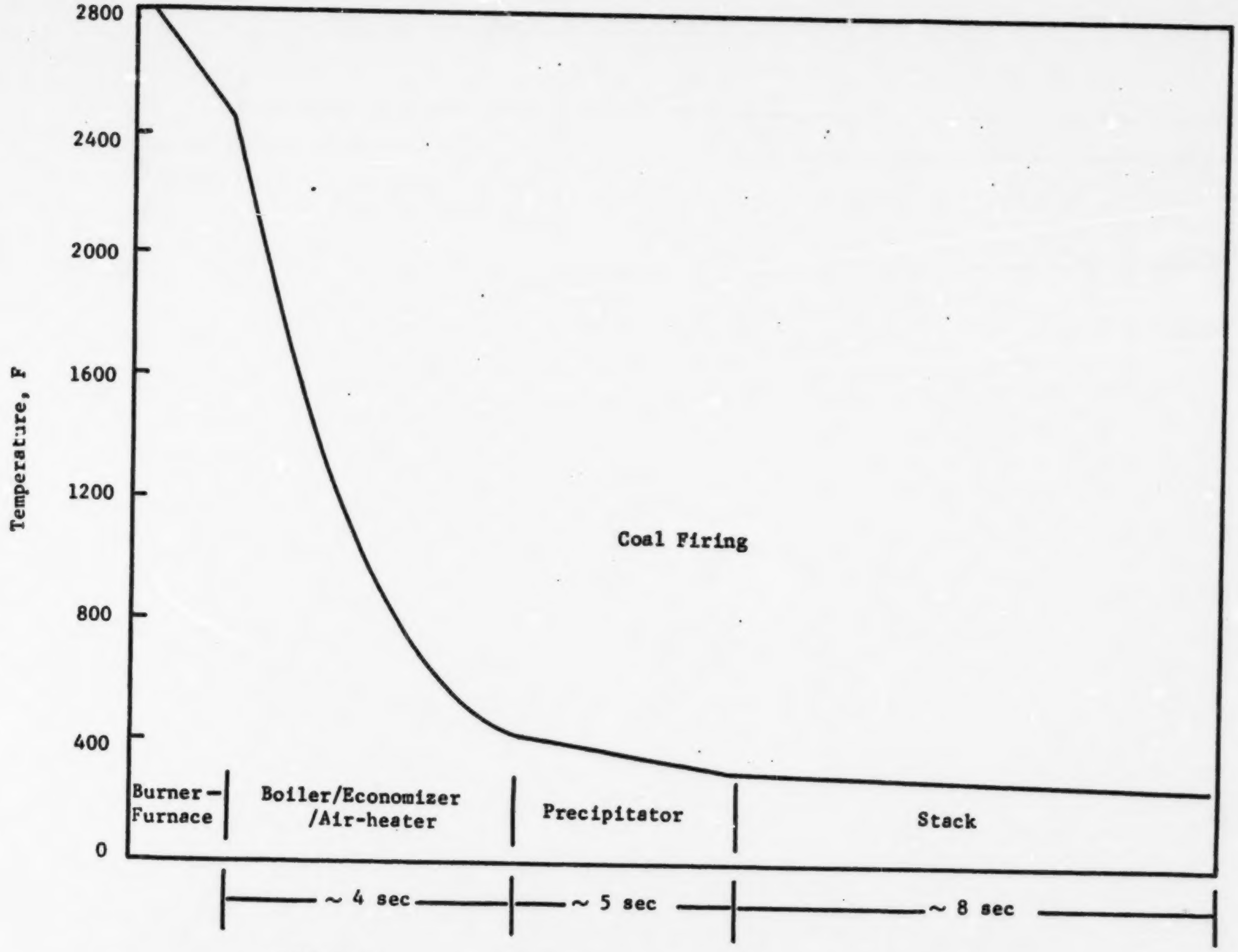


FIGURE 11. TIME-TEMPERATURE PROFILE TYPICAL OF COAL FIRING

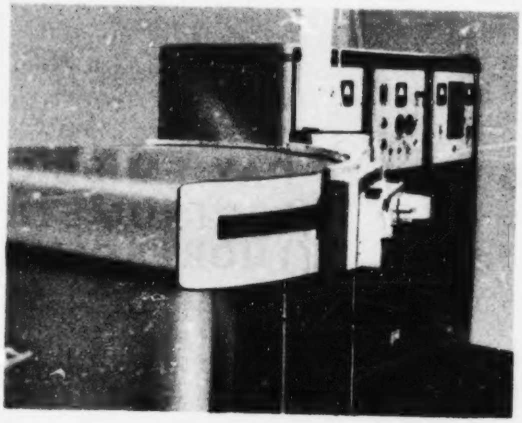


FIGURE 12. OPTICAL EMISSION SPECTROGRAPHY (OES)

Battelle's emission spectrographic laboratory is equipped with a 1.5 meter, 25,000 line/inch grating instrument. The spectra are recorded on photographic film in the region 2200A to 9400A and the dispersion in the second order is 3.5A/mm. Samples for analysis are routinely handled in solid form, as powders and as liquids. The system can detect some 70 elements qualitatively and quantitatively to a precision of about 3 percent. However, only about 50 elements are determinable at low concentrations. Detection limits for the detectable elements are in the range of 1-100 ppm on a bulk analysis or of the order of 10^{-6} to 10^{-9} grams when analyzing a micro sample.

A strong feature of the emission spectrograph, besides being able to accept materials for analysis in a variety of forms, is that it provides a very rapid method for qualitative and semiquantitative determination of a large number of elements. The arc-spark chamber is equipped for handling samples in inert or oxygen-rich atmospheres where useful.

Ancillary to both the optical and X-ray spectrographs are sample preparation facilities including both wet and dry preparative techniques.

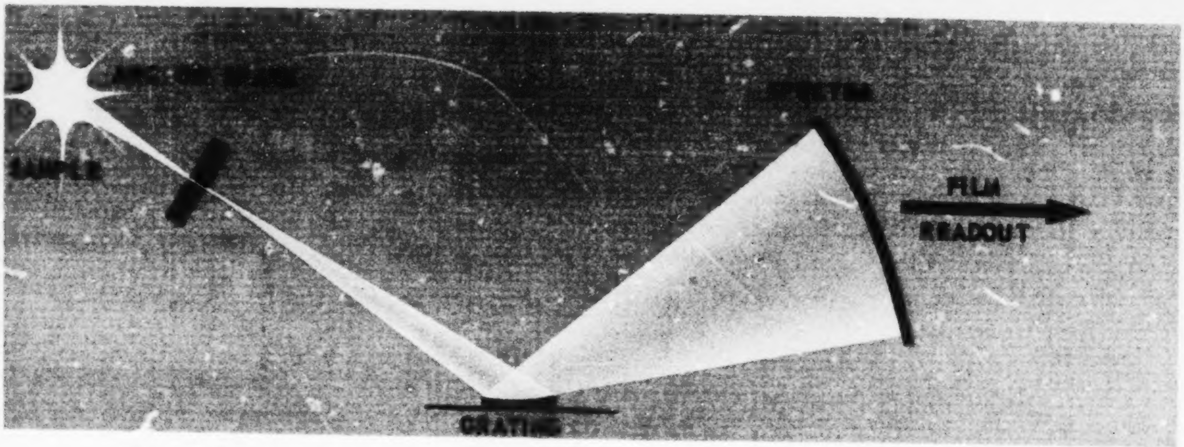


FIGURE 13. SCHEMATIC REPRESENTATION OF OES PRINCIPLE

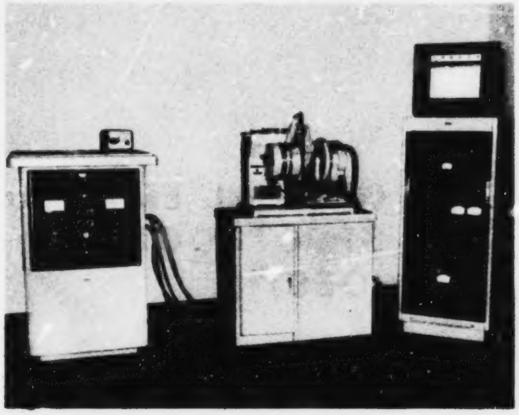


FIGURE 14. X-RAY EMISSION SPECTROMETRY (FLUORESCENCE, XRF)

Battelle's X-ray emission spectrometer is a vacuum instrument capable of detecting and determining elements between atomic number 12 (Mg) and 92 (U) inclusive. It is equipped with A.D.P., PET and LiF analyzing crystals, gas flow and scintillation detectors and sample beam collimaters of 0.005" x 4" and 0.02" x 4. The readout is on strip chart in counts per second and in seconds per count. It can handle samples in form of chunk, powder and liquid and is especially useful for rapid quantitative determination of elements in concentration ranges of 0.01 percent to major amounts. The absolute sensitivity when looking at a single element is of the order of 10^{-6} g. The precision of the analyses provided is of the order of 1 percent.

Ancillary to both the optical and X-ray spectrographs are sample preparation facilities including both wet and dry preparative techniques.

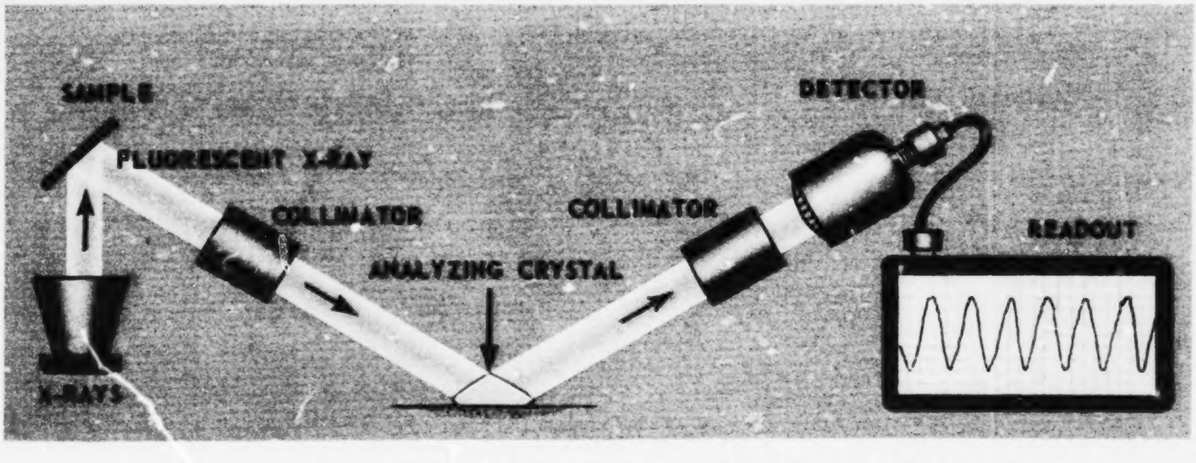


FIGURE 15. SCHEMATIC REPRESENTATION OF XRF PRINCIPLE

C, H, N Analyses

Carbon, hydrogen, and nitrogen analyses were made on a Perkin-Elmer Model 240 Elemental Analyzer. This is an automated instrument combining the classic Pregl and Dumas techniques. The combined analyses for C, H, and N are obtained on single samples of 1 to 3 mg of materials ranging from high-melting organic solids to highly volatile liquids.

Wet Chemical Analysis for S

Sulfate sulfur was determined gravimetrically by precipitation as barium sulfate in a solution which had been acidified and boiled to expel H_2S, SO_2.

Total sulfur was determined gravimetrically by precipitation as barium sulfate in a solution which has been treated with bromine and nitric acid to convert all sulfur to sulfate.

The details of procedure for these wet chemical methods are given in Appendix B .

Goksøyr-Ross Procedure (G/R) for SO_3 and SO_2

Figure 16 shows the Goksøyr-Ross coil. The flue gases, reasonably cleaned of particulate by a glass wool plug, are drawn through a glass coil and a Grade 4 sintered glass disc, both enclosed in a water-filled jacket. The water is maintained at a temperature (60-90 C) well below the acid dew point but is slightly above the water dew point. Practically all the sulfuric acid condenses on the walls of the coil. Any acid mist particles left in the gas stream are retained by the sintered glass filter. The acid is then washed out and determined by titration with standard sodium hydroxide solution.

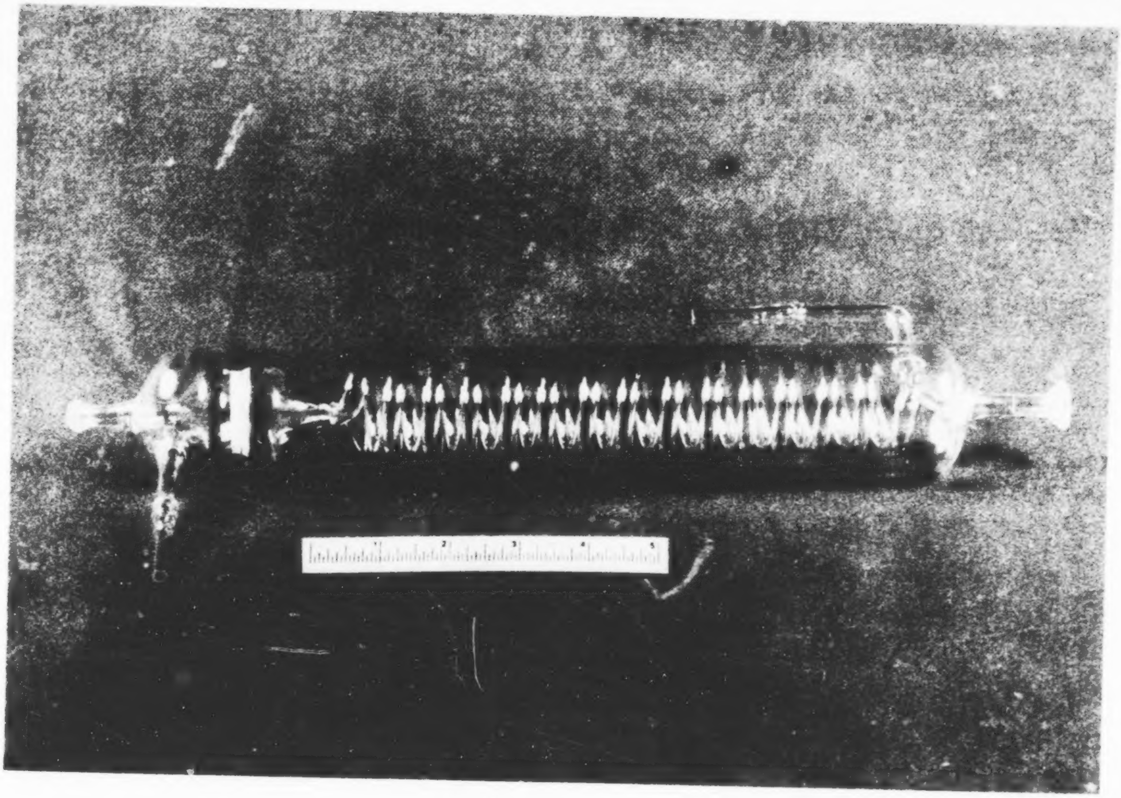


FIGURE 16. GOKSØYR ROSS COIL

The gas sample flows from right to left. In the exit chamber is visible a fritted glass disc which stops most of the residual acid mist that may escape condensation on the coil wall. (Also widely referred to as the Shell-Thornton coil.)

The gases leaving the sulfur trioxide collector are then passed through hydrogen peroxide solution; all the sulfur dioxide is converted to sulfuric acid which is titrated with standard sodium hydroxide solution.

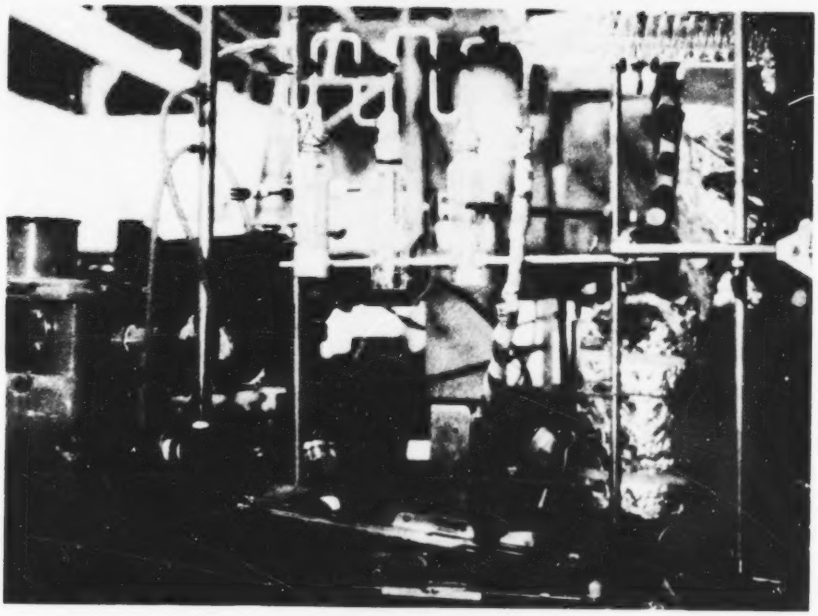
Figure 16.1 shows the sulfuric acid coil in two applications: in (a) the coil is in use in the analysis train described by Goksøyr and Ross, and in (b) a larger version of the coil is shown in places between the filter and impingers of an EPA sampling train. The white material visible in the inlet end of the coil is the sulfuric acid mist formed in the coil during particulate sampling at Edgewater Power Station (see Run 51 in Table 12).

Experimental Details and Results

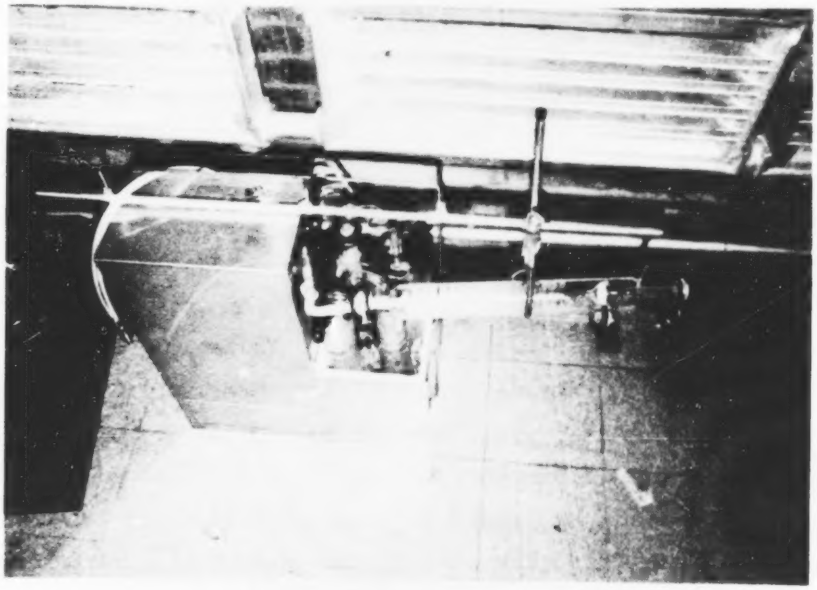
Initial Trials

In these trials, samples were collected from the Multifuel Furnace Facility during oil-fired operation in order to obtain information on particulate from residual-oil fuels and to examine several alternatives in sampling and analyses procedures that were under consideration. The samples were collected from Port P-1, see Figures 8 and 17, using a Vycor probe about 8 in. long. Both silver and MSA glass 1106 BH filter materials were tried at temperatures of 230 and about 400 F using the EPA sampling train. The results for these experiments are summarized in Table 2.

The filter samples were stored over indicating Drierite and weighed several times. Because of the heterogeneous mixtures of organic and other condensibles that might collect on the filter, each in small amount, the most suitable handling of the filter was not known. For these trials a procedure was employed in which the filter was divided into halves; one for homogenizing by grinding for elemental analyses by means of optical emission spectrometry and X-ray fluorescence and the other for extraction by benzene and dilute sulfuric acid. The amounts of material



(a)
Sulfuric acid coil in analysis train with H_2O_2 bubblers for SO_2



(b)
Sulfuric acid coil adapted for use in EPA train, between filter and impingers

FIGURE 16.1. GOKSØYR-ROSS PROCEDURE

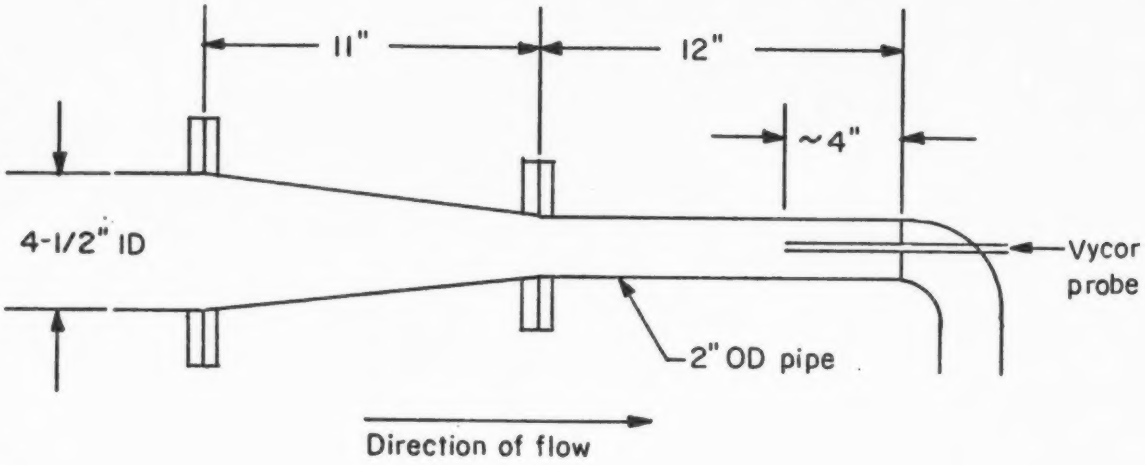

11"
12"
~4"
4-1/2" ID
Vycor probe
2" OD pipe
Direction of flow

FIGURE 17. SCHEMATIC VIEW OF SAMPLE PORT P-1, SEE FIGURE 8

TABLE 2. INITIAL TRIALS, RESULTS FROM OIL-FIRED LABORATORY BURNER

Run No.	4		5		6		7		8	
Date	4/26		4/26		4/27		4/28		5/4	
Materials										
Probe	Vycor		Vycor		Vycor		Vycor		Vycor	
Filter	Silver		MSA glass 1106 BH		Silver		MSA glass 1106 BH		MSA glass 1106 BH	
Oil	Venezuelan 954		Venezuelan 954		Venezuelan 954		Mid Continent		Mid Continent	
Temperatures										
Stack	465		465		510 F		490 F		435	
Filter	230		400-370		390		230		400	
Impinger	68		68		65		64		71	
Sample										
Gas Vol., m^3	0.173		0.275		0.286		0.422		0.422	
Mass, mg	(a)		(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)
Probe	NA		15.2	5.5	36.7	17.3	145.1	23.5	62.7	12.8
Filter	22.9		28.6		22.6		74.0		24.4	
Impinger	NA		29.8	10.5	78.1	20.4	32.6	12.5	75.0	30.0
TOTAL	NA		73.6	44.6	137.4	60.3	251.7	110.0	162.2	67.2
Analysis of Filter (OES)	(c)	(d)	(c)	(d)	(c)	(d)	(c)	(d)	(c)	(d)
Li	--		--	--	--	--	0.16	0.3	0.07	0.15
B	Trace		0.4	1.3	--	--	1.00	3.0	0.20	0.6
Na	0.18	0.2	2.0	2.7	0.18	0.24	5.00	6.8	5.80	7.8
Mg	0.11	0.2	0.8	1.3	0.11	0.18	2.00	3.3	0.40	0.7
Al	0.68	1.3	1.2	2.3	0.68	1.28	3.00	5.7	0.60	1.1
Si	0.08	0.3	?	?	0.08	0.26	?	?	?	?
K	--	--	0.6	0.7	0.12	0.14	1.60	1.9	0.40	0.5
Ca	0.11	0.2	2.0-4.0	4.2	0.11	0.15	5.0-10.0	10.5	1.0-2.0	2.1
Ti	Trace	Trace	Trace	Trace	0.01	0.02	--	--	--	--
V	1.20	2.1	3.8	6.8	2.4	4.3	0.96	1.7	0.96	1.7
Cr	0.12	2.0	0.25	0.4	0.12	0.18	0.31	0.5	0.23	0.3
Mn	--	--	0.01	Trace	Trace	Trace	0.01	Trace	Trace	Trace
Fe	0.05	0.1	0.04	0.1	0.11	0.15	0.42	0.6	0.02	Trace
Ni	0.19	0.2	0.26	0.3	0.19	0.24	0.32	0.4	0.24	0.3
Co	Trace	Trace	--	--	Trace	Trace	Trace	Trace	Trace	Trace
Cu	0.01	Trace	0.02	Trace	0.01	0.01	--	--	Trace	Trace
Sr	--	--	--	--	--	--	0.03	Trace	0.01	Trace
Zr	0.01	Trace	Trace	Trace	0.01	0.01	--	--	--	--
Mo	Trace	Trace	0.01	Trace	0.01	0.01	Trace	Trace	Trace	Trace
Sn	--	--	--	--	0.05	--	--	--	--	--
Ba	Trace	Trace	0.03	Trace	Trace	Trace	0.04	Trace	0.05	Trace
Pb	0.02	Trace	0.02	Trace	0.02	Trace	0.06	0.1	0.02	Trace
S (XRF)	NA	NA	8.8	22.0	NA	NA	NA	NA	8.4	21.0
V (XRF)	NA	NA	3.0	5.4	NA	NA	NA	NA	1.96	3.5
TOTAL				40.7						39.0

FOOTNOTES FOR TABLE 2

(a) Filter weight after desiccation; probe and impinger samples obtained by evaporation H_2O layer 230 F, evaporation organic layer, 75 F.

(b) Probe and impinger residues resulurried in acetone, refiltered onto weighed Tissuquartz filter, dry 170 F.

(c) Optical emissions spectra (OES) and X-ray fluorescence spectra (XRF) analysis; results in mg of element contained in total filter catch.

(d) Oxide weights equivalent to OES and XRF analyses; results in mg of oxide/filter.

(e) NA indicates not obtained.

removed in these extractions were expected to yield estimates of organic material (benzene soluble), and carbonate or nitrate contents (acid decomposed).

The high background provided by the glass filter for the major elements of the fly ash resulted in a high degree of uncertainty in the fly-ash analyses. For this reason a brief investigation was made of suitability of a high-purity quartz filter as a substitute for the glass. Tissuquartz 2500 QAO was obtained and compared with MSA glass 1106 BH filter on the basis of weight, surface area, fiber diameter, and elemental composition. These results are summarized in Tables 3 and 4.

TABLE 3. COMPARISON OF GLASS AND QUARTZ FILTER MATERIALS

	Filter	
	Tissuquartz QAO 2500	MSA Glass 1106BH
Weight taken (6 $in.^2$), g	0.265	0.263
Dried He, 150 C, 1 hr, g	0.245	0.263
Heated in air, 450 C, 1 hr, g	0.242	0.262
Derived Properties		
Moisture as received, wt %	8	0
Loss due to oxidation, wt %	1	~0
Surface Areas, BET		
After He, 150 C, m^2/g	4.0	1.7
After air, 450 C, m^2/g	6.3	2.1
Derived Property		
Effective fiber diameter, μ	0.3 - 0.5	1.1 - 0.9

Note: Tissuquartz QAO 2500 obtained from Pallflex Products Corporation, Putnam, Connecticut 06260

MSA Glass 1106BH obtained from Mine Safety Appliances Company, Pittsburgh, Pennsylvania 15208

TABLE 4. OES ANALYSES (± 50%) FOR IMPURITIES IN GLASS AND QUARTZ FILTER MATERIALS

	Micrograms/3-inch Circle,	
	Tissuquartz	MSA Glass
Li	< 3	--
B	6	2200
Na	30	11000
Mg	150	4400
Al	150	6600
K	16	3200
Ca	300	11000 to 22000
Ti	16	22
V	< 3	< 2
Cr	trace	6
Mn	< 3	4
Fe	30	220
Ni	--	2
Cu	16	10
Sr	16	--
Zr	--	22
Ba	< 3	22
Pb	< 30	4

The probe and impinger catch were collected by washing the respective portions of the apparatus with water, acetone, and methylene chloride. For the impinger portions, these washings were added to the 100 cc of water used in each of the first two impingers. In each case, the water layer was separated from the organic layer portion and dried in an oven at 110 C. Then, the organic portion was added to the same dishes and dried at room temperature. After the bulk of liquid had evaporated, the dishes were put into a desiccator to dry to a constant weight. Weighings made on successive days showed that no further loss of liquid was occurring by evaporation. However, the weights bore no systematic relation to the volume of gas sampled and so each of the probe and impinger residues was reslurried in acetone and the insoluble residues were filtered onto Tissuquartz 2500 QAO filter material. Because the fly-ash material would be expected to have low solubility in acetone, the change in residue weight obtained in this way provided a preliminary estimate of the nonfly ash part of the probe and impinger portions. The results for these trials are summarized in Table 5.

Table 5 shows that substantial, and apparently arbitrary changes could be produced in the weight of particulate by the choice of drying conditions. The acetone extraction was not valid as it removed inorganic materials and H_2SO_4 that should remain. The weights from this treatment thus should be too low. The slow and more or less continuous loss of water as the particulate temperature was raised illustrated the difficulty in recognizing when all free water had been removed and only combined water remained. In the absence of a clear-cut distinction between these two water forms, the choice among various drying temperatures was arbitrary. As free water should be rapidly lost at 212 F, and in view of the weight changes observed, the drying treatment at 210-220 F was preferred.

Recognition of the analytical uncertainties resulting from the use of glass filters, and the large effects of the choice of drying conditions on sample weight led to the design of a new series of trials intended to permit comparison of some alternative choice of collection condition. The decision corresponded in time with conversion of the Multifuel

TABLE 5. EFFECT OF DRYING TREATMENTS UPON APPARENT MASS OF PARTICULATE SAMPLES

		Weight Collected After Drying,(a) mg			
		75 F	Acetone-Extract	175-180 F	210-220 F
Run 5	Probe	15.2	5.5	13.4	11.1
	Filter	28.6	(28.6)(b)	(28.6)(b)	(28.6)(b)
	Impinger	29.8	10.5	23.6	21.6
	Total	73.6	44.6	65.6	61.3
Run 6	Probe	36.7	17.3	34.0	29.0
	Filter	22.6	(22.6)(b)	(22.6)(b)	(22.6)(b)
	Impinger	78.1	20.4	79.1	64.1
	Total	137.4	60.3	135.7	115.7
Run 7	Probe	145.1	23.5	115.5	113.5
	Filter	74.0	(74.0)(b)	(74.0)(b)	(74.0)(b)
	Impinger	32.6	12.5	25.2	21.3
	Total	251.7	110.0	214.7	208.8
Run 8	Probe	62.7	12.8	50.2	43.6
	Filter	24.4	(24.4)(b)	(24.4)(b)	(24.4)(b)
	Impinger	75.0	30.0	73.4	65.6
	Total	162.2	67.2	148.0	133.6

(a) The four columns of data pertain to four different drying treatments:

75 F = evaporate and desiccate at room temperature over Drierite

Acetone Extract = extract above with acetone, weigh insoluble residue

175-180 F = evaporate acetone and dry residue at 175-180 F

210-220 F = heat above for 1 hour or more at 210-220 F.

(b) Filter samples after desiccation, not further processed, see Table 2.

Furnace to coal-fired operation (for the purposes of another program for which the furnace was built) so that oil-fired sampling was not continued. The first series of experiments on coal-fired operation of the Multifuel Furnace was thus undertaken.

Experimentation Using the Multifuel Furnace, Coal-Fired Operation

The coal fired was from Harrison County, West Virginia, see Table 6 for analysis.

TABLE 6. ANALYSES OF COAL USED IN MULTIFUEL FURNACE FACILITY, WEIGHT PERCENT

	Coal Identification	
	3078[a]	3077[b]
H_2O	1.3	1.44
C	68.8	76.6
H	5.01	5.45
N	1.2	1.4
S	3.5	3.00
Ash	15.4	7.3
$O_{\text{(by difference)}}$	4.4	4.8

[a] 3078 = Unwashed Pittsburgh bed.
3077 = Washed Pittsburgh bed.

These coals were from the Robinson Run Mine of Consolidation Coal Company near Shinnston (Harrison County), West Virginia.

The sampling conditions were chosen so as to correspond to the array of experiments outlined in Table 7. Under the operating conditions, the stack gas temperature at the sampling point upstream of the precipitator was about 550-650 F and so the probe temperatures listed in Table 7 were used as a guide for adjustment of minimum temperatures in the probe. In those runs where 400 F probe was specified, temperatures were maintained at 400 F or greater until the gases entered the filter holder portion of the apparatus. In those runs where 250 F probe temperatures were called for, the probe was allowed to cool to this temperature at a point preceding the filter-holder portion. Where the G/R-type coil was used, it was intended to collect the H_2SO_4 vapors that otherwise might accumulate in downstream portions of the apparatus and so might have altered the acidity of those portions. The acid thus collected was washed out of the coil and combined with the probe or impinger catch, after the run was completed, depending on whether the coil was before or after the filter holder, respectively. In this way the coil represented a special portion of a probe or impinger used for these research purposes.

The procedure for particulate analysis for this series of trials is shown in Figure 18. It included C, H, and N analyses which were to be used as the basis for interpreting the carbon-containing portion of the particulate. For the filter-catch portion of the sample a series of C, H, and N analyses was included. Thus, after obtaining a total of C, H, and N analysis on an aliquot, a portion of the filter catch was extracted with benzene, dried, and the C, H, and N analyses were determined on this portion. The relatively large amount of benzene used was expected to remove all organic materials, and the difference in the two C, H, and N analyses was called organic material. A portion of the residue from benzene extraction was then extracted using aqueous H_2SO_4 and the extraction was assumed to remove water-soluble inorganic material and decompose all carbonates and nitrates. The change in C, H, and N analysis due to this extraction was interpreted as due to carbonates and nitrates. The C residue left after acid extraction included elemental carbon and was referred to as such.

TABLE 7. PLAN FOR A SERIES OF EXPERIMENTAL PARTICULATE COLLECTIONS FROM THE LABORATORY COAL-FIRED FURNACE SYSTEM

Run No.	Collection Conditions(1)						Objective: Comparison of					
	Gases	Probe		Filter		Coil	Probe (2)	Filter (3)	Acidity (4)	Time (5)	Dilution	
		250F	400F	230F	400F						(6)	(7)
A	S	316SS		Q		No	x					
B	S	Inconel		Q		No	x					
C	S	Q		Q		No	x					
D	S		Q	Ag		No		x				
E	S		Q	G		No		x				
F	S		Q	Q		No		x	x			
G	S		Q		Q	No			x			
H	S		Q		Q	Yes			x	x	x	x
I	S(8)		Q		Q	Yes				x		
J	S:AIR 1:10(10)		Q		Q	Yes					x	x
K	S		Q		Q	Yes(9)						x

(1) The symbols are as follows: S = Stack gas, Q = Quartz or Vycor, G = Glass, Ag = Silver.

(2) To examine acceptability of metal probes under "wet" collection conditions.

(3) To compare influence of available filter materials under "wet" collection conditions.

(4) To examine changes as major acid collection is shifted from filter to coil to impinger.

(5) To examine effect of residence time of particulate in sample train.

(6 and 7) To examine dilution effects - in (6) the effect of O_2 and dew point on mass collected, in (7) the effect of dew point at filter is emphasized.

(8) Total gas flow rate $\frac{1}{2}$ that of runs A-H, but time of collection is doubled.

(9) The coil is before the filter in this case; otherwise it is between filter and impingers.

(10) Total flow rate is same as in runs A-H, K.

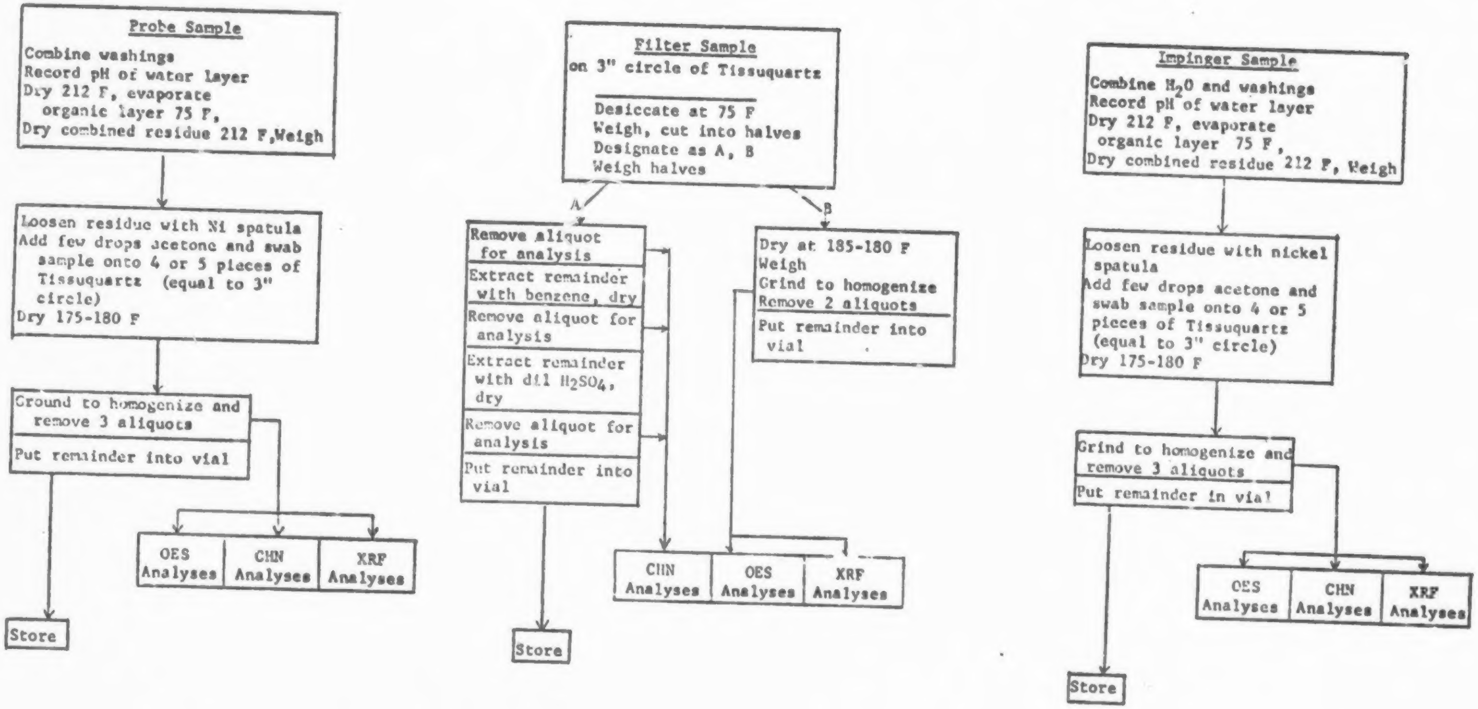
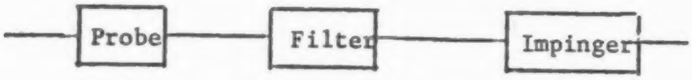

Probe Sample
Combine washings
Record pH of water layer
Dry 212 F, evaporate organic layer 75 F,
Dry combined residue 212 F,Weigh
Loosen residue with Ni spatula
Add few drops acetone and swab sample onto 4 or 5 pieces of Tissuquartz (equal to 3" circle)
Dry 175-180 F
Ground to homogenize and remove 3 aliquots
Put remainder into vial
OES Analyses
CHN Analyses
XRF Analyses
Store
Filter Sample
on 3" circle of Tissuquartz
Desiccate at 75 F
Weigh, cut into halves
Designate as A, B
Weigh halves
A
B
Remove aliquot for analysis
Extract remainder with benzene, dry
Remove aliquot for analysis
Extract remainder with dil H_2SO_4, dry
Remove aliquot for analysis
Put remainder into vial
Store
Dry at 185-180 F
Weigh
Grind to homogenize
Remove 2 aliquots
Put remainder into vial
CHN Analyses
OES Analyses
XRF Analyses
Impinger Sample
Combine H_2O and washings
Record pH of water layer
Dry 212 F, evaporate organic layer 75 F,
Dry combined residue 212 F, Weigh
Loosen residue with nickel spatula
Add few drops acetone and swab sample onto 4 or 5 pieces of Tissuquartz (equal to 3" circle)
Dry 175-180 F
Grind to homogenize and remove 3 aliquots
Put remainder in vial
OES Analyses
CHN Analyses
XRF Analyses
Store

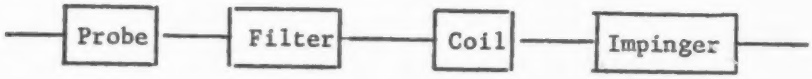
FIGURE 18. FLOW CHART OF ANALYTICAL PROCEDURE FOR PARTICULATE SAMPLES FROM COAL-FIRED OPERATION OF LABORATORY FURNACE

The experimental series outlined in Table 7 was carried out using three basic arrangements of apparatus:

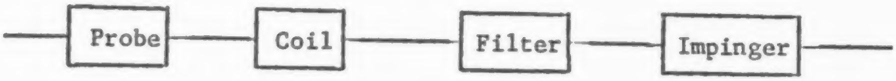
For modes A-C



For modes H-J



For mode K



The results for these trials are summarized in Table 8. Their significance is discussed under Discussion of Results.

The benzene and acid extraction of the filter catch were discontinued after several had been completed. The relatively thick filter samples obtained from coal-fired operation tended to flake off during extraction of some samples and thereby ruined the accuracy needed. In addition, the total C, H, and N analyses for probe, filter, and impinger portions, listed in Table 8, indicated that in many cases only a minor part of the carbon in the particulate was found in the filter portion. The results for one sample from oil-fired operation and two samples from coal-fired operations are listed in Table 9. These results indicate the nature of the analytical data for samples where handling difficulties were minimal.

The data of Table 8 were used to make detailed material balances so that the effects of these experimental variations in sampling mode could be studied. The material balances and conclusions are discussed in a later section along with the results of the other trials, see Discussion of Results.

TABLE 8. ANALYTICAL DATA FOR PARTICULATE COLLECTION FROM COAL-FIRED LABORATORY BURNER

Run No.		9				10				11				12				13				14			
Date		6/16/71				6/17/71				6/18/71				6/18/71				6/23/71				6/23/71			
Materials																									
Probe		Short Vycor				Short Vycor				Short Vycor				Short Vycor				Inconel				316 SS			
Filter		Tissuquartz QAO 2500				Tissuquartz QAO 2500				Silver				MSA Glass 1106 BH				Tissuquartz QAO 2500				Tissuquartz QAO 2500			
Coal	(a)	3078				3078				3078				3078				3077				3077			
Temperatures, F																									
Stack		630				630				580				550				630				640			
Probe	(b)	~400				~400				~400				~400				240				240			
Filter		225				400				245				230				230				235			
Impinger		70				74				72				83				72				71			
Coil	(c)	--				--				--				--				--				--			
Sample																									
Gas Vol., m^3		0.463				0.516				0.370				0.322				0.392				0.601			
Sampling Mode	(d)	F				G				D				E				B				A			
	(e)	P	F	I	T	P	F	I	T	P	F	I	T	P	F	I	T	P	F	I	T	P	F	I	T
pH	(f)	<2.0		2.0		3.8		2.2		7.9		2.4		2.8		2.4		3.4		3.0		3.2		2.5	
Mass, mg	(g)	186	202	101	489	990	282	533	1805	284	312	153	749	79	160	111	350	567	235	77	879	501	292	74	867
O.E.S., mg	(h)																								
	Li	0.01	0.02	--	0.03	0.65	0.12	0.01	0.78	0.06	(i)	--		T	(j)	--		0.35	0.11	--	0.46	0.24	0.03	--	0.27
	B	0.02	0.10	T	0.12	0.13	0.11	0.08	0.32	0.04		0.02		0.01		T		0.26	0.27	0.01	0.54	0.24	0.30	T	0.54
	Na	0.36	0.39	--	0.74	5.2	1.14	0.42	6.8	1.15		0.43		0.36		0.18		4.3	1.06	0.35	5.4	2.4	0.40	0.72	3.5
	Mg	0.42	0.95	0.10	1.47	5.1	1.7	0.84	7.6	1.7		0.16		0.69		0.15		4.3	2.1	0.12	6.5	4.0	1.7	0.30	6.0
	Al	2.4	5.0	0.14	7.5	26.	12.	2.6	40.	8.7		0.32		1.47		0.20		26.	10.7	0.14	37.	24.	8.9	0.32	33.
	K	1.4	1.5	0.04	2.9	19.	4.7	0.86	25.	3.5		0.31		0.37		0.19		17.	1.6	0.25	19.	4.0	0.40	0.25	4.6
	Ca	2.3	4.9	0.32	7.5	13.	5.7	4.2	23.	5.7		0.70		1.65		1.01		8.6	7.9	0.88	17.	11.9	1.0	0.88	13.8
	Ti	0.37	0.50	--	0.87	6.4	1.7	0.34	8.5	1.2		0.02		0.14		0.01		2.6	1.6	0.02	4.2	2.4	0.29	0.01	2.7
	V	0.01	0.05	--	0.06	0.26	0.12	--	0.38	0.03		--		--		--		0.61	0.21	--	0.82	0.32	0.12	--	0.44
	Cr	0.05	0.10	--	0.15	0.90	0.29	0.04	1.23	0.12		0.07		0.02		0.01		2.6	0.32	0.01	2.9	3.2	0.18	0.01	3.4
	Mn	0.01	0.02	--	0.03	0.13	0.06	0.04	0.23	0.04		T		T		--		0.17	0.05	T	0.22	0.32	0.04	--	0.36
	Fe	4.8	5.0	0.18	10.0	26.	8.7	8.7	43.	11.7		0.30		1.87		0.26		8.7	8.0	0.15	17.	15.	2.9	0.16	19.
	Ni	0.02	0.02	0.04	0.08	0.09	0.04	0.03	0.16	0.04		0.01		0.01		0.01		2.6	0.02	0.01	2.6	1.6	0.01	0.01	1.6
	Co	--	--	2.0	2.0	0.03	0.01	1.73	1.8	0.01		0.01		--		0.03		0.02	0.01	0.03	0.06	0.02	--	T	0.02
	Cu	0.03	0.03	0.02	0.13	0.64	0.28	0.08	1.0	0.28		0.03		0.01		0.02		0.16	0.09	0.01	0.26	0.15	0.11	0.01	0.27
	Sr	0.04	0.09	0.01	0.14	0.26	0.08	0.11	0.45	0.11		0.01		0.01		0.01		0.86	0.26	0.01	1.13	0.40	0.11	0.01	0.52
	Zr	0.01	0.03	--	0.04	0.13	0.06	--	0.19	0.03		--		0.01		--		0.09	0.04	0.01	0.14	0.08	--	--	0.08
	Mo	--	0.01	--	0.01	0.01	0.01	--	0.02	--		--		--		--		0.03	0.01	--	0.04	0.24	0.01	--	0.25
	Ag	--	--	--	--	--	0.01	--	0.01	0.01		--		--		--		0.09	0.01	--	0.10	T	--	T	T
	Sb	--	--	--	--	0.13	0.12	--	0.25	--		--		--		--		--	--	--	--	--	--	--	--
	Ba	0.09	0.24	--	0.33	0.93	0.40	0.16	1.5	0.34		--		0.85		--		0.86	1.06	T	1.9	1.6	0.05	0.01	1.7
	Pb	--	--	--	--	0.13	0.06	--	0.19	0.06		0.05		0.43		0.04		0.43	0.11	0.08	0.62	0.40	--	0.08	0.48
Total		12.39	18.94	2.85	34.18	105.12	37.41	20.24	162.77	34.82		2.44		7.90		2.12		80.63	35.53	2.09	118.25	73.51	16.55	2.77	92.83
XRF, mg	(l)																								
	Al	6.9	9.4	0.18	16.5	91.	32.5	4.3	127.8	21.6	(i)	0.6		2.7	(j)	0.3		34.7	21.7	0.09	56.5	33.	19.6	0.09	52.7
	K	3.5	4.0	2.6	10.1	40.	12.	2.3	54.3	13.9		0.02		1.37		0.22		30.5	4.8	0.19	35.5	10.	4.3	0.15	14.5
	Ca	2.5	8.1	4.1	14.7	31.3	10.	3.6	44.9	8.5		0.25		1.47		1.1		12.9	9.2	0.31	22.4	13.8	9.2	0.38	23.4
	Ti	0.57	1.0	0.18	1.8	7.2	2.5	0.49	10.2	1.8		0.07		0.27		0.01		3.6	2.4	0.03	6.0	3.7	2.7	--	6.4
	V	0.11	0.15	0.04	0.3	0.75	0.23	0.27	1.3	0.18		0.06		0.03		0.04		0.4	0.27	0.03	0.7	0.42	0.23	0.03	0.7
	Fe	10.4	12.7	0.56	23.7	135.	40.	10.4	185.4	37.		0.67		3.9		0.45		5.7	26.0	0.28	32.0	63.5	25.	0.3	88.8
	Cu	0.15	0.15	0.12	0.4	0.82	0.25	0.16	1.2	0.23		0.02		0.07		0.02		0.27	0.22	0.02	0.5	0.48	0.22	0.02	0.7
	Pb	--	--	--	--	--	--	--	--	--		--		--		--		--	--	--	--	--	--	--	--
Total		24.1	35.5	7.8	67.4	306.1	97.5	21.5	425.1	83.2		1.7		9.8		2.1		88.1	64.6	1.0	153.7	124.9	61.3	1.0	187.2
S	(m)	28.3	39.8	19.4	87.5	26.9	6.3	41.6	74.8	4.5	(i)	13.9		13.8	(j)	10.7		32.	24.1	7.1	63.2	37.5	46.5	6.5	90.5
Combustion, mg	(n)																								
	C	8.0	1.0	13.2	22.2	2.9	0.5	4.0	7.4	17.7	7.2	3.0	27.9	9.2	(k)	7.2		4.7	0.4	12.0	17.1	2.9	0.8	7.0	10.7
	H	4.7	nil	3.0	7.7	3.2	0.5	11.7	15.4	--	5.3	8.9	14.2	2.4		8.1		---	3.7	6.6	10.3	1.0	6.9	2.3	10.2
	N	0.4	0.1	0.9	1.4	--	0.1	0.2	0.3	0.4	0.3	3.9	4.6	0.2		0.5		0.2	0.1	0.7	1.0	0.1	0.3	1.0	1.4

TABLE 8. ANALYTICAL DATA FOR PARTICULATE COLLECTION FROM COAL-FIRED LABORATORY BURNER (Contd)

Run No.		15				17				18				19				23				24			
Date		6/23/71				6/25/71				6/25/71				6/25/71				7/14/71				7/14/71			
Materials																									
Probe		Long Quartz				Short Vycor				Short Vycor				Short Vycor				Short Vycor				Short Vycor			
Filter		Tissuquartz QAO 2500				Tissuquartz QAO 2500				Tissuquartz QAO 2500				Tissuquartz QAO 2500				Tissuquartz QAO 2500				Tissuquartz AQO 2500			
Coal		3077				3077				3077				3077				3077				3077			
Temperatures, F	(a)																								
Stack		590				640				610				570				750				720			
Probe	(b)	~240				~400				~400				~400				230				390			
Filter		230				395				400				230				230				230			
Impinger		75				72				71				67				74				72			
Coil	(c)	--				184				172				176				--				--			
Sample																									
Gas Vol, SCF		11.9				0.336				0.632				0.386				0.332				0.327			
Sampling Mode	(d)	C				H				I				K				C				F			
	(e)	P	F	I	T	P	F	I	T	P	F	I	T	P	F	I	T	P	F	I	T	P	F	I	T
pH	(f)	2.7		2.3		3.2		2.8		3.1		2.2		2.6		2.2		3.1		2.6		3.10		2.35	
Mass, mg	(g)	203	168	133	504	130	132	43	305	116	155	194	465	131	118	70	319	358	214	87	659	189	190	35	414
O.E.S., mg	(h)																								
	Li	0.05	0.03	--	0.08	0.04	0.05	--	0.09	0.05	0.09	--	0.14	0.01	0.01	--	0.02	2.0	0.05	--	2.1	0.05	0.1	--	0.15
	B	0.05	0.32	0.04	0.41	0.08	0.37	0.01	0.46	0.10	0.45	0.02	0.57	0.03	0.42	0.01	0.46	0.1	0.26	0.01	0.37	0.1	0.25	0.01	0.36
	Na	0.99	0.92	0.28	2.2	0.84	0.51	1.0	2.35	1.5	1.4	0.23	3.1	0.28	0.28	0.35	0.91	9.9	1.5	0.2	11.6	1.5	1.5	0.1	3.1
	Mg	1.45	1.36	0.26	3.1	2.1	5.3	0.15	7.6	2.1	5.3	0.18	7.6	0.37	1.2	0.11	1.7	4.6	3.6	0.4	8.6	3.4	2.9	0.4	6.7
	Al	10.0	9.3	0.39	20.	4.3	5.3	0.15	9.8	3.6	6.8	0.21	10.6	2.1	2.9	0.14	5.1	9.9	10.3	0.2	20.4	9.8	9.8	0.1	19.7
	K	1.5	0.93	0.20	2.6	0.85	1.05	0.23	2.1	1.0	2.3	0.24	3.5	0.21	0.41	0.10	0.72	2.6	2.1	0.4	5.1	2.0	2.0	0.2	4.2
	Ca	4.8	6.8	0.65	12.2	4.1	7.8	1.5	13.4	5.0	6.6	0.80	12.4	2.8	3.8	0.52	7.1	9.9	10.3	0.4	20.6	9.8	9.8	0.4	20.0
	Ti	0.49	0.93	0.01	1.4	0.85	1.6	T	2.5	1.0	1.4	0.02	2.4	0.21	0.41	0.01	0.63	1.0	1.0	0.02	2.0	1.0	1.0	0.02	2.0
	V	0.10	0.14	--	0.24	0.13	0.05	--	0.18	0.05	0.18	--	0.23	0.01	0.04	--	0.05	0.07	0.2	--	0.27	0.05	0.2	--	0.25
	Cr	0.15	0.09	0.01	0.25	0.22	0.16	T	0.38	0.15	0.23	0.01	0.39	0.02	0.03	0.01	0.06	0.3	0.4	--	0.7	0.3	0.3	--	0.6
	Mn	0.04	0.03	--	0.07	0.02	0.05	--	0.07	0.03	0.05	T	0.08	T	0.01	--	0.01	0.03	0.04	--	0.07	0.03	0.03	--	0.06
	Fe	5.0	4.7	0.20	9.9	4.3	5.3	0.14	9.7	5.1	4.5	0.23	9.8	2.1	4.2	0.09	6.4	13.2	10.3	0.2	23.7	9.8	9.8	0.1	19.7
	Ni	0.02	0.01	0.01	0.04	0.03	0.03	0.01	0.07	0.03	0.02	0.01	0.06	0.01	0.01	0.01	0.03	0.03	0.05	--	0.08	0.05	0.05	--	0.1
	Co	--	--	0.02	0.02	T	T	0.01	0.01	T	0.01	--	0.01	0.01	--	0.01	0.02	0.01	0.01	0.01	0.03	0.01	0.01	0.02	0.04
	Cu	0.08	0.07	0.02	0.17	0.02	0.09	--	0.11	0.09	0.07	0.03	0.19	0.02	0.02	0.02	0.06	0.2	0.2	0.1	0.5	0.1	0.1	0.07	0.27
	Sr	0.14	0.23	0.03	0.40	0.12	0.20	0.01	0.33	0.20	0.22	0.04	0.46	0.07	0.07	0.02	0.16	0.3	0.4	0.04	0.74	0.2	0.5	0.03	0.73
	Zr	0.03	0.05	--	0.03	0.02	0.03	--	0.05	0.03	0.05	T	0.08	0.01	0.02	T	0.03	0.03	0.03	--	0.06	0.02	0.03	0.01	0.06
	Mo	--	0.01	--	0.01	--	0.15	--	0.15	0.01	0.03	--	0.04	--	0.01	--	0.01	0.01	0.01	--	0.02	0.01	0.02	--	0.03
	Ag	--	--	--	--	T	T	T	T	T	--	T	T	--	--	--	--	T	--	T	T	--	--	--	--
	Sb	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	0.3	0.04	0.04	0.74	0.2	0.5	0.03	0.73
	Ba	0.24	0.46	T	0.70	0.21	0.52	T	0.73	0.08	0.20	0.01	0.29	0.08	0.20	0.01	0.29	1.3	0.8	0.02	2.1	0.5	0.7	0.02	1.22
	Pb	0.15	0.09	0.04	0.28	0.13	0.11	0.10	0.34	--	0.08	0.04	0.12	--	0.08	0.04	0.12	0.3	0.3	0.04	0.64	0.1	0.3	--	0.4
Total		25.28	26.47	2.16	53.91	18.36	28.67	3.31	50.34	20.12	29.98	2.07	52.17	8.34	14.12	1.45	23.91	56.1	42.2	2.1	100.4	39.0	39.9	1.5	80.4
XRF, mg	(l)																								
	Al	9.1	13.4	0.27	22.8	7.4	16.8	0.15	24.4	8.5	14.6	0.08	23.2	3.1	3.1	0.085	6.3	17.3	19.	0.18	36.5	14.8	19.6	0.09	34.5
	K	2.5	2.7	0.01	5.2	2.7	4.2	1.9	8.8	2.6	3.8	0.08	6.5	1.2	1.3	0.03	2.5	5.5	4.8	0.7	11.0	4.1	5.1	0.6	9.8
	Ca	4.2	6.0	0.42	10.6	3.7	8.4	0.48	12.6	3.9	7.6	0.16	11.7	1.4	2.7	--	4.1	6.5	7.6	0.1	14.2	5.3	8.6	0.1	14.0
	Ti	0.9	1.6	0.025	2.5	0.88	1.95	0.09	2.9	0.87	1.9	0.025	3.0	0.4	0.63	0.05	1.1	1.7	1.9	--	3.6	1.36	2.0	--	3.4
	V	0.15	0.15	0.05	0.3	0.21	0.24	0.015	0.5	0.15	0.19	0.08	0.4	0.10	0.09	0.026	0.2	0.2	0.18	0.03	0.4	0.14	0.18	0.03	0.4
	Fe	15.	15.3	0.2	30.5	13.	20.4	0.24	33.6	4.6	17.3	0.31	22.2	6.0	5.9	0.2	12.1	27.6	21.5	0.21	49.3	22.5	23.6	0.2	46.3
	Cu	0.08	0.13	--	0.2	0.07	0.13	0.03	0.2	--	0.11	--	0.11	0.09	0.10	0.04	0.2	0.35	0.09	0.03	0.5	0.2	0.15	0.03	0.4
	Pb	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	0.6	--	--	0.6	--	--	0.38	0.4
Total		31.9	39.3	1.0	72.2	28.0	52.1	2.9	83.0	20.6	45.5	0.7	65.8	12.3	13.8	0.5	26.6	59.8	55.1	1.3	116.1	48.4	59.6	1.1	109.2
S, mg	(m)	24.6	23.8	6.7	55.1	9.1	8.	6.9	24.0	11.7	9.6	15.3	36.6	22.	28.6	6.1	56.7	19.7	26.6	9.2	55.5	13.6	15.5	8.9	38.0
Combustion, mg	(n)																								
	C	1.6	0.3	4.3	6.2	2.4	0.4	11.9	14.7	7.0	1.7	8.9	17.6	1.8	0.5	3.9	6.2	34.7	1.0	2.2	37.9	7.2	0.8	1.5	9.5
	H	2.6	3.9	9.1	15.6	0.3	0.4	1.9	2.6	0.6	1.3	11.6	13.5	3.5	7.2	5.4	16.2	1.3	3.1	8.0	12.4	0.4	1.7	3.4	5.5
	N	0.2	0.1	0.6	0.9	0.2	--	1.0	1.2	0.4	0.3	1.4	2.1	0.3	0.1	1.1	1.5	--	0.1	0.6	0.7	0.1	0.1	0.9	1.1

TABLE 8. ANALYTICAL DATA FOR PARTICULATE COLLECTION FROM COAL-FIRED LABORATORY BURNER (Contd)

Run No.		26				28				29				31			
Date		7/14/71				7/15/71				7/15/71				7/15/71			
Materials																	
Probe		Short Vycor				Short Vycor				Short Vycor				Short Vycor			
Filter		Tissuquartz QAO 2500				Tissuquartz QAO 2500				Tissuquartz QAO 2500				Tissuquartz QAO 2500			
Coal	(a)	3077				3077				3077				3077			
Temperatures, F																	
Stack		680				570				640				560			
Probe	(b)	390				~400				~400				~400			
Filter		395				405				405				230			
Impinger		72				69				65				69			
Coil	(c)	--				163				174				174			
Sample																	
Gas Vol., m^3		.406				0.310				0.685				0.389			
Sampling Mode	(d)	G				H				I				K			
	(e)	P	F	I	T	P	F	I	T	P	F	I	T	P	F	I	T
pH	(f)	4.30		2.25		4.60		2.55		4.60		2.65		2.9		2.8	
Mass, mg	(g)	418	208	142	768	149	274	94	517	340	311	628	1.279	409	95	60	564
O.E.S., mg	(h)																
	Li	0.2	0.15	--	0.35	0.05	0.1	--	0.15	0.1	0.1	0.1	0.3	0.1	0.01	--	0.11
	B	0.2	0.25	0.01	0.46	0.05	0.2	0.01	0.26	0.1	0.2	0.1	0.4	0.07	0.16	0.01	0.24
	Na	2.9	1.5	0.1	4.5	0.9	1.7	0.4	3.0	1.9	1.8	1.9	5.6	2.1	0.3	0.03	2.4
	Mg	5.0	4.1	0.4	9.5	0.9	1.7	0.4	3.0	1.9	0.6	2.8	5.3	2.8	0.8	0.4	4.0
	Al	21.5	15.2	0.2	36.9	6.7	11.5	0.2	18.4	12.8	18.3	13.9	45.0	21.3	1.6	0.02	22.9
	K	7.2	2.5	0.04	9.7	2.2	5.7	0.2	8.1	6.4	0.6	2.8	9.8	7.1	0.4	0.01	7.6
	Ca	14.3	10.2	1.3	25.8	4.5	8.6	2.0	15.1	9.6	12.2	13.9	35.7	14.2	5.9	1.1	21.2
	Ti	1.4	1.0	0.02	2.4	0.5	1.1	0.02	1.6	1.3	1.2	1.4	3.9	1.4	0.3	0.02	1.7
	V	0.7	0.5	--	1.2	0.03	0.1	--	0.13	0.3	0.06	0.03	0.39	0.2	0.02	--	0.22
	Cr	1.4	0.8	--	2.2	0.09	0.2	0.01	0.3	0.4	0.4	0.3	1.1	0.2	0.03	0.01	0.24
	Mn	0.05	0.04	--	0.09	0.02	0.06	--	0.08	0.06	0.06	0.03	0.15	0.07	0.1	--	0.17
	Fe	14.3	10.2	0.3	24.8	9.0	11.5	0.2	20.7	12.8	12.2	18.6	43.6	14.2	4.0	0.03	18.2
	Ni	0.2	0.1	--	0.3	0.02	0.06	--	0.08	0.1	0.06	0.03	0.19	0.04	--	--	0.04
	Co	0.01	0.01	--	0.02	0.01	0.01	0.01	0.03	0.01	0.1	--	0.11	0.01	--	--	0.01
	Cu	0.4	0.2	0.03	0.63	0.05	0.1	0.02	0.17	0.1	0.1	0.1	0.3	0.1	0.4	0.02	0.16
	Sr	0.7	0.3	0.04	1.0	0.1	0.3	0.04	0.44	0.3	0.3	0.4	1.0	0.4	0.08	0.04	0.52
	Zr	0.05	0.03	--	0.08	0.02	0.06	0.01	0.09	0.06	0.06	0.05	0.17	0.07	0.01	--	0.08
	Mo	0.02	0.03	--	0.05	--	0.02	--	0.02	0.01	0.04	0.01	0.06	0.01	--	--	0.01
	Ag	T	T	--	T	--	--	--	--	T	--	--	T	--	--	T	T
	Sb	0.7	0.3	0.04	1.0	0.1	0.3	0.04	0.44	0.3	0.3	0.4	1.0	0.4	0.08	0.04	0.52
	Ba	0.7	0.8	0.02	1.5	0.2	0.3	0.01	0.51	0.3	0.4	0.4	1.1	0.4	0.2	0.01	0.61
	Pb	0.6	0.3	0.04	0.94	0.2	0.2	0.2	0.6	0.5	0.5	0.6	1.6	0.2	0.04	0.07	0.31
Total		72.5	48.5	2.5	123.5	25.6	43.8	3.8	73.2				156.8				81.2
XRF, mg	(1)																
	Al	29.4	16.6	0.28	46.3	14.5	31.	0.19	45.7	31.2	33.2	10.	74.4	36.9	4.4	0.14	41.4
	K	11.	5.0	--	16.0	6.1	11.8	2.9	20.8	13.5	13.9	6.8	34.2	15.8	2.3	0.025	18.1
	Ca	11.	6.2	0.34	17.5	4.5	10.7	0.24	15.4	10.8	11.9	6.3	29.0	11.1	3.3	0.29	14.7
	Ti	3.2	0.85	--	4.0	1.1	2.4	--	3.5	2.5	2.7	1.5	6.7	2.6	--	0.31	2.9
	V	0.64	0.69	--	1.3	0.085	0.22	--	0.3	0.33	0.3	0.32	1.0	0.27	--	0.05	0.3
	Fe	59.	5.7	0.68	65.4	19.	35.5	0.3	54.8	44.	41.3	27.5	112.8	38.4	5.8	0.48	44.7
	Cu	0.38	0.24	0.03	0.7	0.06	0.13	0.02	0.2	0.14	0.28	0.17	0.6	0.15	0.1	0.02	0.3
	Pb	2.0	--	--	2.0	0.06	1.2	--	1.3	0.07	2.1	--	2.2	0.08	0.06	--	0.1
S, mg	(m)	9.7	6.1	8.8	24.6	4.6	6.6	7.2	18.4	7.1	6.0	74.5	87.6	38.0	17.3	4.5	59.8
Combustion, mg	(n)																
	C	17.6	3.6	2.0	23.2	3.2	8.6	4.0	15.8	3.5	1.3	1.2	6.0	6.4	9.2	1.5	17.1
	H	--	0.7	9.3	10.0	--	0.9	3.7	4.6	--	0.7	8.2	8.9	--	3.3	4.3	7.6
	N	--	0.1	0.7	0.8	0.2	0.4	0.2	0.8	--	0.1	0.5	0.6	0.1	0.3	0.5	0.9

FOOTNOTES FOR TABLE 8

(a) The coals used are identified as follows:

3077 Pittsburgh Bed, washed, S = 3.0%
ash = 7%
3078 Pittsburgh Bed, unwashed, S = 3.5%
ash = 13%.

(b) Probe temperature was controlled by specifying the temperature for the coolest portion just preceding the filter chamber. The inlet end of the probe is at stack temperature.

(c) Used to remove H_2SO_4 vapor, but no frit was used to retain mist so that particulate collections would not be altered. The location of the coil is specified by the sampling mode.

(d) Sampling mode refers to the alphabetized listing of runs in Table 7 of this report. Gas samples volumes are expressed in cubic meters at 1 atmosphere and 20 C.

(e) The letters in this row are column headings -

P = Probe
F = Filter
I = Impinger
T = Total.

(f) pH obtained on the water layer after being combined with H_2O used for washing.

(g) Weight of the total catch after drying at 212 F.

(h) Analysis results for weights of elements found by optical emission spectroscopy. Because of the filter material Si could not be determined with an accuracy better than ± 50 percent.

(i) The silver filter requires a different handling procedure and was not analyzed at this time.

(j) The high background for many elements in the glass filter used in this experiment makes this analysis meaningless in the present work.

(k) The glass filter material is not suitable for use in the C-H-N combustion train.

(l) X-ray fluorescence analyses for selected elements.

(m) Obtained by XRF and represents all forms of sulfur present.

(n) Carbon, hydrogen, and nitrogen combustion train analyses.

TABLE 9. COMPARISON OF C, H, N CONTENTS FOLLOWING EXTRACTION OF FILTER PORTIONS WITH BENZENE AND WITH AQUEOUS ACID

Run	Element	Total, mg	After C_6H_6 Extraction, mg	After C_6H_6 and then Aqueous Acid, mg
4[a]	C	0.19	0.22	0.14
	H	0.12	0.12	0.02
	N	0.02	0.02	0.02
9[b]	C	1.0	1.0	0.9
	H	nil	5.5	0.6
	N	0.1	0.1	nil
11[b]	C	7.2	7.0	6.2
	H	5.3	0.5	1.0
	N	0.3	0.3	0.1

(a) Oil-fired operation, see experimental data, Table 2.

(b) Coal-fired operation.

The methods for handling of fly ash, and the analytical requirements, had become fairly well established as a result of the earlier series of trials. However, basic problems remained to be explored for the sulfur oxide portion of the catch. For this reason, a series of trials was conducted to determine the magnitude of SO_2 retention and oxidation during sampling and during subsequent handling of the samples. This series, made by sampling gases from the Battelle Multifuel Furnace using coal, is described in this section. A subsequent series made at Edgewater Power Station, also using coal, at Lorain, Ohio, utilized the experience gained in handling the sulfur oxide portion and is described in the following section.

For these experiments, the objective was to compare the total sulfur oxide contents of the stack gas, as determined by the Goksøyr-Ross procedure, with the sulfur oxide retained in a series of impingers. More explicitly, the objective was to compare the SO_3 content of the stack gas with the SO_3 found in the impingers and to note any contribution of SO_2 to the total sulfur retained in the impingers.

The sulfate normally found in the evaporated residue of impinger catch solutions can originate by oxidation of SO_2 at any of several stages in the sampling and analysis procedure. Thus, the sulfate found may be the sum of

(1) SO_3 present in the stack gas
(2) SO_3 generated during sampling (here 40 minutes)
(3) SO_3 generated in the impinger solutions during storage under air in bottles, and transported to the laboratory (usually days or weeks)
(4) SO_3 generated during sample evaporation and analysis.

The data for this series provides a comparison of the magnitude of (1), measured by the Goksøyr-Ross procedure, with the sum of all four, measured several ways in this work but comparable to the range of conditions normally encountered in sampling processing.

The experimental procedures used can be understood with the help of the schematic representation of the experimental plan shown in Figure 19. Details of the configuration used for each run and data for these trials are presented in Table 10. For these trials, only the sulfur analyses for the components contained inside the dashed line were of interest. The coal used was Number 3077 which is Pittsburgh Bed Coal, washed, S = 3.0% and ash = 7% (see Table 6).

The first four impingers used in this series of experiments each contained 100 ml of water or aqueous solution. Impinger 5 shown in Figure 19 was empty. To determine the possibilities for oxidation of SO_2 to SO_3, the total catch of SO_3 in the four impingers was compared for different experimental conditions, and the relative concentration of SO_3 in each of the four impingers was examined for evidence of a continuing production of SO_3 during collection, storage, and analysis.

The liquid from the impingers and the wash water were bottled and kept separate from the subsequent washings with acetone and methylene chloride. Only the water phase of the impingers was analyzed for sulfur in this series. The analysis of the probe samples represents the total sulfate and sulfite sulfur retained after evaporation of the water layer at 210-220 F and subsequent 75 F evaporation of the organic washings. The filter analysis represents the material as collected at 250 F and subsequently stored over P_2O_5.

Sulfate in impinger solutions was determined by making the solution strongly acid by adding 15 ml of 6 N HCl to a 50-100-ml aliquot and heating to drive off the SO_2. The residual sulfate was measured

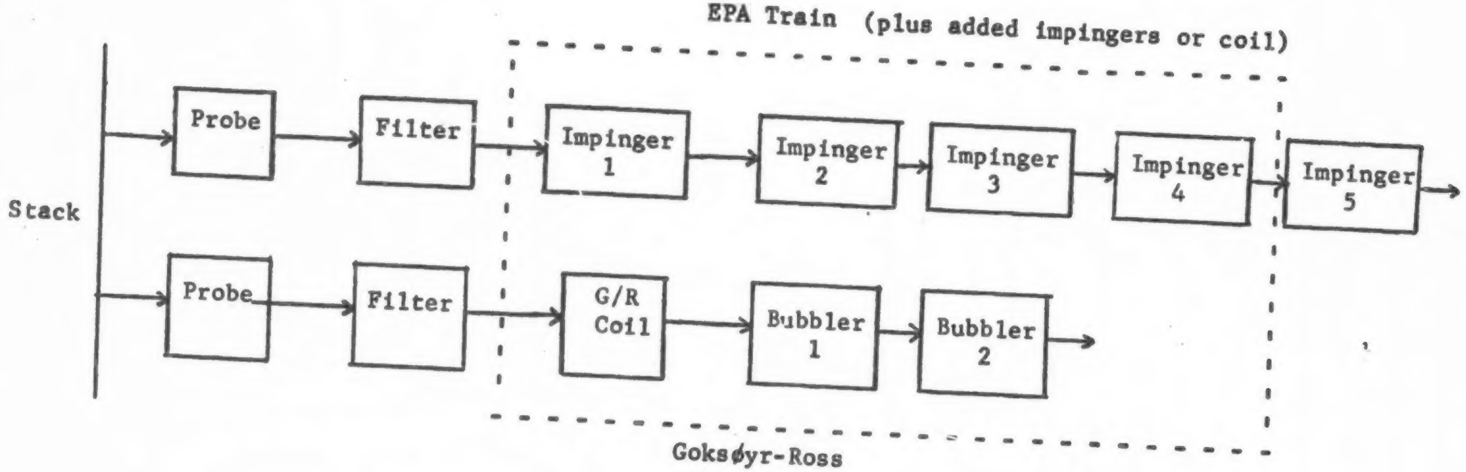

EPA Train (plus added impingers or coil)
Stack
Probe
Filter
Impinger 1
Impinger 2
Impinger 3
Impinger 4
Impinger 5
Probe
Filter
G/R Coil
Bubbler 1
Bubbler 2
Goksøyr-Ross

FIGURE 19. SCHEMATIC REPRESENTATION OF THE EXPERIMENTAL APPARATUS FOR INVESTIGATION OF SO_2 AND SO_3

TABLE 10. OXIDATION OF SO_2 DURING SAMPLING OF STACK GASES FROM BATTELLE MULTIFUEL FURNACE UNDER VARIOUS CONDITIONS. (OXYGEN CONTENT OF STACK GASES APPROXIMATELY 4 PERCENT, SAMPLE TAKEN BEFORE ELECTROSTATIC PRECIPITATOR)

Run	38			39			40			41			42			43		
Date	9/17/71			9/17/71			9/17/71			9/17/71			9/29/71			9/29/71		
Temperature, F																		
Stack	375			375			375			375			370			370		
Probe	380			400			400			400			400			410		
Filter	250			250			240			255			250			255		
Impinger	64			70			64			67			72			74		
G/R Coil(a)	163			162			174			177			161			163		
Gas, Volumes, m^3																		
Coil	0.126			0.145			0.161			0.163			0.212			0.200		
EPA Train	0.406			0.507			0.340			0.338			0.416			0.391		
Experimental Mode(b)	I			II			III			I			I			IV		
Particulate, mg(c)	mg		mg/m^3	mg		mg/m^3	mg		mg/m^3	mg		mg/m^3	mg		mg/m^3	mg		mg/m^3
Filter	208		512	192		378	126		370	113		334	214		515	182		465
Probe	130		520	67.3		133	55.0		162	36.5		108	(d)		(d)	(d)		(d)
Results, mg S/m^3													as collected(e)					
	as SO_3	as $SO_2^{(j)}$	Total	as SO_3	as $SO_2^{(j)}$	Total	as SO_3	as $SO_2^{(j)}$	Total	as SO_3	as $SO_2^{(j)}$	Total	as SO_3	as $SO_2^{(j)}$	Total	as SO_3	as $SO_2^{(j)}$	Total
G/R Procedure(f)	15.5	2820	2836	26.8	2740	2769	30.4	2360	2390	35.7	2400	2490	41	2849	2890	43	2850	2890
Probe(f)	10.2	2.5	12.7	6.0	4.9	10.9	6.7	5.6	12.3	26.1	1.4	27.5	--	--	--	--	--	--
Filter(f)	20.5	4.2	24.7	21.5	6.0	27.5	30	4.6	34.6	30.0	6.7	36.7	12.7	--	11.7	10.6	--	10.6
Impingers(g)																		
1	12.0	49	61	9.5	53	63	15.5	162	178	15.5	70	85	4.9	34	38.8	15.9	19	35
2	5.3	88	93	4.6	88	93	8.5	222	231	8.5	169	177	10.2	39	49	14.1	42	56
3	6.7	92	99	30	269	299	81(h)	276(h)	357(h)	9.9	181	191	13.4	33	46	16.2	37	53
4	8.8	92	101	29	265	294	9.5	174	184	9.5	156	166	17.0(i)	85	102	23	37	60
Impinger Total	32.8	321	354	73.1	675	749	114.5	834	950	43.4	576	619	45.5	151	236	69.2	135	204
Ratio Impingers / Stack	2.11	0.11	0.12	2.74	0.25	0.27	3.78	0.35	0.40	1.22	0.24	0.25	1.10	0.067	0.082	1.46	0.046	0.071
													acidified(e)					
Impingers																		
1													10.9	31	42			
2													6.7	35	42			
3													13.1	36	49			
4													15.5	62	78			
Impinger Total													46.2	164	211			
Ratio Impingers / Stack(f)													1.12	0.059	0.074			

FOOTNOTES FOR TABLE 10

(a) Refers to temperature of water circulated through jacket of G/R coil used for SO_3 (or H_2SO_4) collection in parallel with the particulate train.

(b) Experimental modes for the particulate train

I First four impingers each have 100 ml H_2O. The fifth is empty and the sixth contains Drierite.

II The first two impingers each have 100 ml H_2O and the second two have potassium phthalate buffer in H_2O at pH - 5.5. The fifth and sixth impingers are as in I.

III The first four impingers each have 100 ml H_2O as in I, but 76 mg of filter catch from Run 37 was added to the third impinger. (See also Footnote h). The fifth and sixth impingers as above.

IV The first four impingers each have 100 ml 0.1 N HCl. The fith and sixth impingers as above.

(c) Filter catch collected at 250 F and stored in desiccator until weighed. Water wash of probe dried at 212 F and organic wash added and dried at 75 F. Gas volumes are cubic meters calculated at 20 C and 1 atmosphere.

(d) Not analyzed.

(e) The portion labeled "as collected" was analyzed within 24 hours without any further treatment. That labeled "acidified" had 3 ml of 6 N HCl added as soon as it was collected and separated from the other half of the impinger solutions. Samples analyzed within 24 hours.

(f) The probe for the particulate collection and the inlet to the G/R train were both at about 400 F. The SO_2 and SO_3 contents for the G/R procedure are determined directly by titration; for probe and filter the sulfate and totals were determined by XRF and the SO_2 determined by difference. The catch of the G/R procedure is assumed to represent the sulfur analysis of the stack gases being sampled.

(g) Impingers 1 and 3 have open tubes, 2 and 4 are of the Greenfield-Smith type. The total S was obtained by both gravimetric and XRF methods. Good agreement was found for these two analytical methods. Sulfate sulfur was determined gravimetrically and sulfite determined by difference. Analyses for water layer only.

(h) 76 mg of filter catch from Run 37 was added to the third impinger of this run and contributed a total of 5.4 mg S as sulfate and 6.7 mg total sulfur. The values listed in the table are corrected for this contribution.

(i) This impinger contained 200 ml of water initially so as to provide evidence for the influence of the volume of water used.

(j) SO_2 as sulfite sulfur.

gravimetrically as $BaSO_4$. Direct measurement of sulfites in impinger and probe solutions by iodometric titration was not attempted at this time because of the possibility that other species e.g., ferrous iron or organic materials, might contribute to the titration value. Total sulfur was measured as sulfate in two ways: in one method, sulfite was oxidized by bromine and the total measured as $BaSO_4$; in the other, the solution was made alkaline to prevent SO_2 loss and then analyzed as a solution by X-ray fluorescence. These two methods gave very good agreement for the total sulfur estimate.

The probe in the typical Goksøyr-Ross procedure is normally a glass tube that is almost entirely inside the stack and the filter is a small ball of glass wool. The external part of the probe and the glass wool are heated to 400 F. Neither of these parts was analyzed in this series of experiments. Also, the SO_2 effluent from Impinger 4 in the EPA train was not determined.

For the data of Table 10, the Goksøyr-Ross procedure was run simultaneously with the EPA sampling train and for the same period of time. Because the total gas flow through these two systems is different, the results of the table are expressed as mg S (as SO_2 or SO_3) per m^3 gas sampled so that results for the two procedures can be compared directly. In each case, the total sulfur of any kind in an impinger or gas sample can be found by multiplying the mg S/m^3 given by the gas volume sampled.

Field Experiments

Effect of Drying Conditions. Particulate material collected during sampling of exhaust from a cyclone-fired boiler of the Ohio Edison Company at Niles, Ohio, was used to continue the investigation of the hygroscopic nature of some samples. For these samples, the common practice of desiccation over Drierite was abandoned in favor of P_2O_5 as the desiccant.

Table 11 shows data for both water and organic wash layers of probe and impinger catch for two runs. Data are presented showing sample

TABLE 11. EFFECT OF DRYING CONDITIONS ON SAMPLE WEIGHTS-
COAL BURNING OPERATION, NO PRECIPITATOR
(Weights in Grams)

	Initial Evaporation (b)	Desiccate, 24 hr (c)	Heat, 18 hr (d)	Desiccate, 25 hr (c)	Heat, 46 hr (d)	Desiccate, 23 hr (c)	Appearance
Water layer							
Probe							
#1	0.5888	0.5906	0.5865	0.5888	0.5866	0.5881	White and tan solid
#2	0.8425	0.8462	0.8405	0.8452	0.8408	0.8427	White and tan solid
Impinger							
#1	0.2375	0.2417	0.2290	0.2475	0.2237	0.2313	Vitreous dark brown
#2	0.5035	0.5217	0.4917	0.5103	0.4762	0.4882	Vitreous tan, translucent
Organic layer(e)							
Probe							
#1	0.0235	0.0242	0.0184	0.0196	0.0177	0.0185	Black, solid specks
#2	0.0193	0.0202	0.0144	0.0155	0.0151	0.0161	Black, fine solid
Impinger							
#1	0.0032	0.0041	0.0002	0.0015	0.0001	0.0012	Black solid
#2	0.0017	0.0024	0.0000	0.0007	-0.0004(f)	0.0005	Tan solid

(a) Samples collected from Ohio Edison Power Station, Niles, Ohio, cyclone-fired boiler.

(b) For water layer, evaporate to dryness in 212 F oven; organic layer, evaporate at room temperature in air, then heat 2 hours at 155-160 F.

(c) Over P_2O_5 - all dishes in desiccator at one time.

(d) At 212 F, cool 1 hour or less in desiccator before weighing.

(e) Combined acetone and methylene chloride solvent washings.

(f) Erroneous negative weight results from difficulty of weighing small amounts of sample in dishes weighing several grams.

weights after repeated exposure of the samples to alternative periods of heating and desiccation.

The solids recovered from the water layers of the probe catch are tan and white solids similar in appearance to the filter catch and the percentage changes in weight of these solids due to repeated heating and desiccation periods are shown in Table 11 to be quite small (less than 1 percent). The impinger water layers are vitreous in appearance and are slightly more sensitive to drying procedures (maximum variation in weights were about 10 percent)

The residues from the organic layers are black, noncrystalline in appearance and show changes in weight that are greater than 25 percent. However, as the weights of the organic layer residues were only about five percent of weights of the residues from the water layer, these large variations in weight may not appreciably influence the weight of the total sample.

Although based on only a few samples, the differences in the effects of humidity and heat treatment on reproducibility of weighings from Table 11 appear to correlate well with the physical appearance of the residue. Thus, physical appearance may serve as an indicator of sample drying and weighing difficulties and may identify samples that will require analysis for water content.

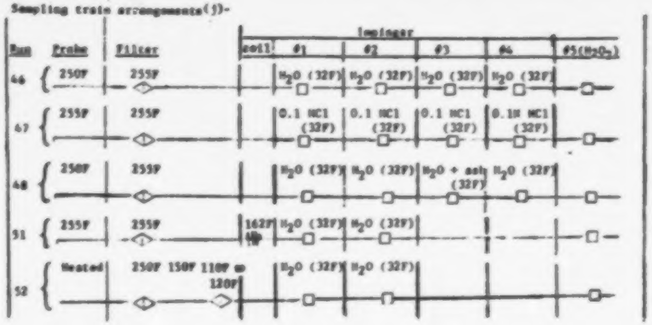
Experiments at Edgewater Power Station. The problem of measurement of the sulfur content of particulate was approached by attempting to account for all of the sulfur in the gases and particles sampled, and to examine the influence of variations in the sampling train configuration on sulfur retention in the various parts of the train.

Table 12 summarizes the sulfur data for several samples collected with various impinger configurations during field sampling on the pulverized

TABLE 12. INVESTIGATION OF THE OXIDATION STATE FOR SULFUR OXIDES RETAINED IN SEVERAL VARIATIONS OF THE PARTICULATE SAMPLING TRAIN (a)

Run and Sulfur Oxide Determined	Date of Sample	Stack Temp., F	Gas Analysis, Percent			PARTICULATE SAMPLER																							GOKSØYR-ROSS METHOD			
						Gas Sample Volume, m^3	Total Particulate Mass,(b) APCO Procedure, milligrams S/m³				Sulfur Oxide Determinations, milligrams S/m³																		Gas Sample Volume m^3	Sulfur Oxide Analyses, milligrams S/m³		
								Filter			Probe Catch(c)			Filter Catch(c)			Coil Wash	Impinger Catch(e)										Grand Totals (e)				
														#1 Filter	Glassware	#2 Filter		#1		#2		#3		#4		Total (d)	#5 H_2O_2					
			H_2O	CO_2	O_2		Probe	#1	#2	Total	Dry	H_2O	Org.		H_2O + Org.			H_2O	Org.	H_2O	Org.	H_2O	Org.	H_2O	Org.					Filter	Coil and Bubbler	Total
46	10/5	355	2.5	11.5	8.5 to 9.0	0.629	20.8	25.4		46.2																			0.211			
SO_3												<.5		1.91				<1.1		0.49		0.49		3.88		4.87		6.78			12.4	12.4
SO_2																											2112				2854	2854
Total											0.81	6.0	nil	33.6				32.5	nil	108.4	nil	98.9	nil	99.2	nil	339.0	2112	2451		0.57	2866	2866
47	10/5	380	3.1	11.5	8.5 to 9.0	0.631	27.2	35.5		62.7																			0.211			
SO_3												2.22		5.30				<0.7		<0.7		3.5		6.0		9.5		17.0			12.4	12.4
SO_2																											2352				2854	2854
Total											0.78	8.83	nil	12.0				20.5	nil	29.7	nil	47.3	nil	51.2	nil	148.7	2352	2522		0.57	2866	2866
48	10/5	370	2.6	11.5	8.5 to 9.0	0.648	99.6	38.5		138.1																			0.211			
SO_3												<0.5		2.15				4.2		7.1		3.53(g)		1.41		16.2		18.4			12.4	12.4
SO_2																											2366				2854	2854
Total											3.07	7.4	nil	2.15				25.8	nil	47.0	nil	48.4(g)	nil	57.6	nil	178.8	2366	2557		0.57	2866	2866
51	10/7	410	5.5	11.5 to 12.0	6.8 to 7.5	0.782	98.2	27.2		125.4																			0.218			
SO_3												1.27		2.54			10.2	0.78		3.9						16.9(h)		18.7			17.3	17.3
SO_2																											2257				2744	2744
Total											5.65	2.93	nil	4.10			10.2	38.6	nil	63.9	0.71					116.5(h)	2257	2384		0.92	2761	2761
52	10/7	370	5.1	11.5 to 12.0	6.0 to 7.5	0.895	45.2	25.8	2.7	73.8																			0.218			
SO_3												0.78		2.58	1.77(i)	0.88		11.3		14.5						25.8		31.8			17.3	17.3
SO_2																											2020				2744	2744
Total											22.2	15.5	nil	3.57	7.95(i)	1.70		73.8	nil	50.1	0.71					124.6	2020	2196		0.92	2761	2761

Sampling train arrangements(j)-



Run
Probe
Filter
Impinger
coil
#1
#2
#3
#4
#5(H_2O_2)
46
250F
255F
H_2O (32F)
H_2O (32F)
H_2O (32F)
H_2O (32F)
47
255F
255F
0.1 HCl (32F)
0.1 HCl (32F)
0.1 HCl (32F)
0.1N HCl (32F)
48
250F
255F
H_2O (32F)
H_2O (32F)
H_2O + ash (32F)
H_2O (32F)
51
255F
255F
162F
H_2O (32F)
H_2O (32F)
52
Heated
250F
150F
110F to 120F
H_2O (32F)
H_2O (32F)

FOOTNOTES FOR TABLE 12

(a) Samples taken from the electrostatic precipitator at the outlet stream at Edgewater Power Station, Lorain, Ohio.

(b) Impinger residues were not determined since sulfur analyses were obtained on the solutions themselves.

(c) The headings for probe, filter, and impinger portion include the terms dry, H_2O, and organic, which pertain to the dry catch water layer and acetone-methylene chloride layer portions of the sample respectively. "H_2O" refers to a 6-7 percent H_2O_2 aqueous solution used in Impinger 5. The impinger water samples were made on aliquots stored in completely filled bottles immediately after the run.

(d) These values are the totals for the first four impingers only.

(e) These values are the grand totals for all portions of the catch.

(f) Goksøyr-Ross procedure. Sample collected simultaneously with particulate sample but using separate train. Although isokinetic conditions were not attempted for this train, the quartz wool plug used to filter particulate from this gas sample was analyzed for total sulfur in order to attempt a total sulfur balance. The probe was a hot, smooth glass tube that contained little material and was not analyzed.

(g) 45.6-mg ash from Run 45 added to the third impinger in this run. The dry residue recovered from this impinger weighed 29 mg and no attempt has been made to correct the sulfur analysis of this impinger for the solid added.

(h) Includes coil.

(i) Includes second cyclone held at 150 F.

(j) Train variations shown schematically

┌—— Probe including cyclone
◇ Filter
/\/\/\— Coil, as in Goksøyr-Ross procedure
—□— Impinger.

coal-fired boilers at the Edgewater Power Plant, Lorain, Ohio. The variations in sampling apparatus are shown schematically below the table.

During the sampling operation, two coals were fired at normal full-load rates for the plant. Partial analyses for these bituminous coals, as received supplied by the Ohio Edison Company are

Dates		10/4 to 10/6/71	10/7 and 10/8/71
Moisture, %	-	4.86	5.09
Ash, %	-	10.91	8.49
Sulfur, %	-	3.24	2.65
Heat Value, Btu/lb	-	12,215	12,706

The gas was sampled from the electrostatic precipitator outlet stream: Runs 46, 47, 48 were made simultaneously using adjacent ports in the rectangular duct leading from the precipitator, and Runs 51 and 52 were a similar pair of simultaneous runs carried out at another time. An adjacent port was used for sampling by the Goksøyr-Ross procedure for measuring the SO_3 and SO_2 concentrations of the flue gas simultaneously with each set of runs. From prior information obtained by plant staff the precipitator efficiency was about 98+ percent.

In order to minimize the weathering and oxidation of impinger water samples, 60-ml aliquots of the combined impinger water and water washings were taken from each impinger of Runs 46, 47, 48 and stored in completely filled bottles until analyzed. The results for the impinger portion of Table 12 are based on those aliquots which, in general, show about the same total sulfur contents as the portions stored conventionally in partly filled bottles, but they exhibit substantially less sulfate contents. The improvement in procedure represented by this change is illustrated in Table 13. The differences in sulfate content confirm the expectation that considerable sulfate is generated during sample storage for transportation to the analytical laboratory.

TABLE 13. COMPARISON OF THE SULFUR CONTENTS OF IMPINGER WATER SAMPLES STORED IN DIFFERENT WAYS

mg S/cc solution

	Sulfate Sulfur		Total Sulfur	
	Conventional (a)	Aliquot (b)	Conventional (a)	Aliquot (b)
Run 46				
Impinger 1	0.019	<0.003	0.05	0.11
2	0.028	0.0025	0.29	0.52
3	0.090	0.0025	0.55	0.45
4	0.039	0.017	0.47	0.43
Run 47				
Impinger 1	0.002	<0.003	0.11	0.08
2	<0.002	<0.003	0.13	0.12
3	<0.003	0.017	0.14	0.22
4	0.054	0.023	0.18	0.20
Run 48				
Impinger 1	0.042	0.025	0.23	0.15
2	0.044	0.040	0.33	0.27
3	0.12	0.017	0.30	0.23
4	0.010	0.008	0.35	0.33

(a) Samples stored approximately 3 weeks in partly filled bottles.

(b) 60-ml aliquots stored in completely filled bottles.

Note: SO_2 can be lost by evaporation and oxidation of the sample if the seal on the bottle is not tight. This seems to be a problem in field samples where storage times for such samples is often longer than desirable. The major evaporation and oxidation losses seem to be in the conventional samples; some caps on aliquot samples were reported to be "not tight" after their return to the laboratory so some loss from these is possible. Analytical uncertainties for these samples are in the second significant figure, so these uncertainties also contributed.

The problem of the collection of the fly-ash portion of the sample was investigated in a separate series of experiments summarized in Tables 14A, 14B, and 14C. For this purpose, the analyses were chosen to emphasize the amounts of the individual cations collected, and, in order to identify any problems in sample fractionation during collection, analyses were attempted on all portions of the sampling rig regardless of the apparent importance of the mass of the catch in that portion.

The experiments shown in Tables 14B and 14C represent pairs of experiments made simultaneously, one on the precipitator inlet stream and one on the outlet stream. Simultaneously, G/R collections were made on both inlet and outlet streams. Two additional sets of G/R collections were made to determine reproducibility (see Runs 53 and 54) but the sample from 54A was lost.

The sample-handling and analytical procedures used for the samples from Edgewater Power Station were varied according to the objectives for each experiment. The following is a description of those procedures for the ten runs made in this field work. The program comprised nearly 300 actual analyses of samples all of which required some form of preparation and/or treatment prior to the analyses.

Each run represented a number of subsamples. These subsamples included particulate catches on both quartz filter material and quartz wool; dry, loose powder from the probe area; water washes and organic washes at and near the probe area; water washes and organic washes of up to four impingers; and some solution washes containing particulate sediments.

The analyses of these collective runs varied slightly as to completeness of the characterizations. For the run series No. 44 (including Runs 44, 49, 50, 55, and 56), a metal analyses was made on all subsamples except the filtered sediments from the solutions and catches on the quartz wool. Either total sulfur and/or sulfate sulfur were obtained on specific subsamples. For the run series No. 46 (including Runs 46, 47, 48, 51,

TABLE 14A. GENERAL DATA FOR RUNS 49, 50, 53, 55, 56

Run	Date	Stack Temp., F	Gas Analysis, percent			Goksøyr-Ross Procedure(c)				Particulate Sample			
			H_2O	CO_2	O_2	Sample, m^3	milligrams/m^3 SO_3	SO_2	Total	Sample Location	Gas Volume, m^3	Probe Temp, F	Filter Box Temp, F
49	10/6/71	380	5.8	11 to 12	8.0 to 8.5	0.173	19.9	2942	2970	Electrostatic Precipitator inlet stream	0.782	255	250
50	10/6/71	350	5.5	11 to 11.5	8.2 to 8.6	0.225	15.5	2493	2511	Electrostatic Precipitator outlet stream	0.694	250	240
55	11/8/71	370	6.0	11.5 to 12.5	7.5					Electrostatic Precipitator inlet stream	0.420	255	255
56	11/8/71	390	5.5	11.5 to 12	7.6 to 8	0.215	17.2	2486	2504	Electrostatic Precipitator outlet stream	0.691	255	250
53A	10/7/71				8.0 to 8.6	0.100	15.2	2892	2907	Electrostatic Precipitator outlet stream, Port A			
53B	10/7/71				7.4 to 8.2	0.111	16.8	2854	2871	Electrostatic Precipitator outlet stream, Port D, 53 A and 53 B run simultaneously			
54B	10/7/71				5.7 to 6.6	0.112	19.8	2585	2617	Electrostatic Precipitator inlet stream, 1.5 hours after 53A and B; Port C			

TABLE 148. DISTRIBUTION OF CHEMICAL ELEMENTS AMONG THE PORTIONS OF PARTICULATE CATCH WITH A DOUBLE FILTER ARRANGEMENT[(a)]

Run and Sample Portion[(b)]	Particulate Sample		Elemental Analysis[(d)], mg/m³																
	Sample Location	Catch, mg/m³	Li	Be	B	Na	Mg	Al	Si	S		K	Ca	Ti	V	Cr	Mn	Fe	Ni
										Total	Sulfate								
Run 49	Electrostatic precipitator inlet stream																		
Probe																			
dry material		2899.		0.014	1.20	9.2	15.2	151.9	459.	97.1		91.8	91.8	9.2	1.91	0.92	0.92	459.	0.60
H_2O wash		191.4		<.0007	0.007	1.3	0.25	0.64	0.071	2.30		0.18	2.5	0.014	<.007	0.007	0.018	0.18	0.007
organic wash		2.47		<.0003	0.004	<.04	0.004	<0.004	0.32			<0.04	0.010	<.004	<.003	<.004	<.004	<.004	<.004
Total Probe		3092.9		0.014	1.21	10.5	15.4	152.5	459.	99.4		92.0	94.3	9.2	1.91	0.92	0.92	459.	0.61
Filters																			
#1		1593.	0.74	0.018	0.35	9.18	5.30	144.8		21.9		35.3	35.3	3.53	0.92	0.74	0.35	180.1	0.18
glassware[(f)]		0.247		<.0004	0.002	0.39	0.035	0.035		1.55		0.035	0.11	<.002	<.002	<.002	<.0007	0.007	<.002
#2		4.24		<.0004	0.004	0.04	0.11	0.35		1.17		0.025	0.11	0.021	<.004	<.004	0.071	<.004	<.004
Total filter		1597.	0.74	0.018	0.36	9.61	5.45	145.2		24.6		35.4	35.5	3.55	0.92	0.74	0.42	180.1	0.18
Impingers																			
#1 H_2O				<.00004	0.001	<.018	0.002	0.002	0.007	70.63	(7.8)	0.004	0.004	<.0004	<.002	<.0004	<.0003	0.002	
#1 organic wash				<.00004	0.0001	<.018	0.035	0.035	0.018	<.14		0.004	0.004	<.0004	<.002	<.0004	<.0003	0.004	
#2 H_2O wash				<.00004	<.0001	<.018	0.004	0.0001	0.002	70.63	(4.6)	0.002	0.004	<.0004	<.002	0.0004	<.0003	0.0001	
#2 organic wash				<.00004	0.0001	<.018	0.0002	0.0002	0.004	<.14		0.002	0.0003	<.0004	<.002	0.0004	<.0003	0.002	
Total for #1 and #2					0.0013		0.041	0.038	0.031	141.26		0.012	0.012			0.0008		0.008	
#3 impinger[(g)]										2059.									
Run 50	Electrostatic precipitator outlet stream																		
Probe																			
dry material		28.6		<.0004	0.002	0.14	0.014	0.007	0.14	2.01		<.035	0.106	<.002	<.002	<.002	<.002	0.004	<.002
H_2 wash		8.8		<.0004	<.004	<.035	0.001	0.004	0.014			<.005	0.014	<.004	<.0004	<.004	<.004	0.007	<.004
organic wash																			
Total Probe		37.4			0.002	0.14	0.015	0.011	0.15	2.01			0.12					0.011	
Filters																			
#1		91.1		<.007	0.035	0.17	0.424	5.30		18.72		1.06	1.24	0.25	0.007	0.011	0.014	2.72	0.011
glassware[(f)]				<.0001	0.001	0.071	0.106	0.004		1.17		<.014	0.07	<.0001	<.0001	<.0001	0.004	0.004	<.004
#2		10.9		<.004	0.014	0.035	0.283	0.318		6.71		0.07	0.85	<.021	<.004	<.004	<.004	0.35	<.004
Total filter		102.0			0.050	0.276	0.813	5.62		26.60		1.13	2.16	0.25	0.007	0.011	0.018	3.07	0.011
Impingers																			
#1 H_2O wash				<.00004	0.007	<.002	0.007	0.0004	0.004	27.5	(1.45)	<.002	0.004	<.0004	<.002	<.0004	<.0002	0.0003	
#1 organic wash				<.00004	0.004	<.002	0.00004	<.0004	0.004	0.57		0.002	0.0002	<.0004	<.002	<.0004	<.0002	0.002	
#2 H_2O wash				<.00004	0.0004	<.002	0.002	0.0007	0.002	77.7	(0.42)	<.002	0.007	<.0004	<.002	<.0004	<.0002	0.0003	
#2 organic wash				<.00004	0.0002	<.002	0.0003	0.0004	0.007	0.07		0.002	0.0003	<.0004	<.002	<.0004	<.0002	0.002	
Total for #1 and #2					0.011		0.0093	0.0015	0.014	105.8		0.004	0.011					0.0051	
#3 impinger[(g)]										1974.									

TABLE 14B. DISTRIBUTION OF CHEMICAL ELEMENTS AMONG THE PORTIONS OF PARTICULATE CATCH WITH A DOUBLE FILTER ARRANGEMENT $^{(a)}$ (Cont'd)

Run and Sample Portion$^{(b)}$	Elemental Analysis,$^{(d)}$ mg/m^3 (Cont'd)														
	Co	Cu	As	Sr	Zr	Mo	Ag	Cd	Sn	Sb	Ba	Hg	Pb	Totals	Totals$^{(c)}$ less Sulfur
Run 49 (Cont'd)															
Probe															
dry material	0.14	0.32	<.32	0.32	0.32	0.071	<.14	<.32	0.32	<.32	0.92	<.014	0.32	1392.	1295.
H_2O wash	0.007	0.14	<.07	<.07	<.07	<.007	<.007	<.07	0.035	<.035	0.014		0.071	7.7	5.4
organic wash	<.004	<.004	<.04	<.04	<.04	<.004	0.004	<.04	<.014	<.018	<.004		<.014	0.34	0.34
Total Probe	0.15	0.46		0.32	0.32	0.071	0.004		0.36		0.93		0.39	1400	1301.
Filters															
#1	.071	0.141	0.176	0.883	0.353	0.106	<.018	<.018	0.176	<.106	0.706	0.018	0.177	441.5	419.6
glassware$^{(f)}$	<.002	0.018	<.018	<.018	<.002	<.002	<.0004	<.018	<.018	<.011	<.002		0.035	2.22	0.67
#2	<.004	<.004	<.021	0.025	<.014	<.004	<.004	<.004	0.021	0.021	<.002	0.0007	0.035	2.00	0.83
Total filter	.071	0.159	0.176	0.908	0.353	0.106			0.197	0.021	0.706	0.019	0.247	445.7	421.1
Impingers															
#1 H_2O wash	<.002	0.0008	<.002	<.002	<.002	<.002	<.00004	<.001	<.001	<.001	0.0002		0.001	70.9	0.025
#1 organic wash	<.002	0.0004	<.002	<.002	<.002	<.002	<.00004	<.001	<.001	<.001	0.0004		0.001	0.10	0.102
#2 H_2O wash	<.002	0.0002	<.002	<.002	<.002	<.002	<.00004	<.001	<.001	<.001	<.0002		0.001	70.8	0.015
#2 organic wash	<.002	0.00004	<.002	<.002	<.002	<.002	<.00004	<.001	<.001	<.001	<.0002		<.001	0.008	0.008
Total for #1 and #2		0.0014									0.0006		0.003	141.8	0.150
#3 impinger$^{(g)}$														2059.	
Run 50 (Cont'd)															
Probe															
dry material	<.002	<.004	<.04	<.04	<.002	<.002	<.0004	<.04	<.014	<.014	0.002		<.014	2.55	0.54
H_2O wash	<.004	0.004	<.04	<.04	<.004	<.004	<.0004	<.04	<.018	<.021	<.004		<.018	0.044	0.054
organic wash															
Total Probe		0.004									0.002			2.59	0.58
Filters															
#1	<.007	<.04	0.071	0.071	0.014	<.007	<.007	<.007	0.028	<.028	<.021	0.014	Trace	30.16	11.44
glassware$^{(f)}$	<.0004	0.0001	<.014	<.014	<.001	<.001	<.0001	<.014	<.007	<.007	0.0001		0.004	1.43	0.26
#2	<.0004	<.04	<.021	0.071	<.014	<.004	<.004	<.004	<.021	0.021	<.021	0.001	0.071	8.77	2.06
Total filter		0.0001	0.071	0.14	0.014				0.028	0.021	0.0001	0.015	0.075	40.36	13.76
Impingers															
#1 H_2O	<.021	0.0004	<.002	<.002	<.002	<.002	<.00004	<.001	<.001	<.001	<.0002		0.001	27.5	0.024
#1 organic	<.002	0.0007	<.002	<.002	<.002	<.002	<.00004	<.001	<.001	<.001	<.0002		<.001	0.58	0.013
#2 H_2O	<.002	0.0004	<.002	<.002	<.002	<.002	<.00004	<.001	0.002	<.001	0.0004		0.001	77.7	0.016
#2 organic	<.002	0.00004	<.002	<.002	<.002	<.002	<.00004	<.001	<.001	<.001	<.0002		<.001	0.72	0.012
Total for #1 and #2		0.0015							0.002		0.0004		0.002	106.5	0.065
#3 impinger$^{(g)}$														1974.	

TABLE 14C. DISTRIBUTION OF CHEMICAL ELEMENTS AMONG THE PORTIONS OF PARTICULATE CATCH WITH A SINGLE FILTER ARRANGEMENT$^{(a)}$

Run and Sample Portion$^{(b)}$	Particulate Sample		Elemental Analysis,$^{(d)}$ mg/m^3															
										S								
	Sample Location	Catch, mg/m^3	Li	Be	B	Na	Mg	Al	Si	Total	Sulfate	K	Ca	Ti	V	Cr	Mn	Fe
Run 55	Electrostatic precipitator inlet stream																	
Probe																		
dry material		3,404		0.01	1.34	13.4	17.0	332.	102.	124.		98.9	102.	13.4	2.0	1.0	1.0	494.
H_2O wash		78		<.004	0.007	0.106	0.011	0.177	0.177	14.1		0.071	4.9	<.004	<.004	.004	.007	0.106
organic wash				<.0001	<.001	<0.014	<.0001	<.001	.004			<.014	<.001	<.001	<.001	<.001	<.001	.001
Total Probe		3,482		0.01	1.35	13.5	17.1	332.	102.	138.		99.0	107.	13.4	2.0	1.0	1.0	494.
Filter		614	.007	.014	.49	.71	2.4	67.1		27.5		13.1	12.4	2.6	0.25	0.25	0.14	67.1
Impinger																		
#1 H_2O wash				<.00004	0.004	<.004	0.001	0.001	0.004	88.3	(10.6)	0.007	0.007	<.0004	<.004	0.0004	<.0004	0.004
#1 organic wash				<.00004	.0004	<.004	.00007	<.004	.018	0.25		.004	.0004	<.0004	<.004	<.0004	<.0004	<.0004
#2 H_2O wash				<.00004	<.0004	<.004	.001	.0007	.004	208.	(0.95)	.004	.007	<.0004	<.004	<.0004	<.0004	.0004
#2 organic wash				<.00004	.002	.011	.007	.011	.018	0.95		.007	.011	.0004	<.004	.0007	<.0004	.018
Total for #1 and #2					.0068	.011	.009	.012	.044	297.5		0.022	.025	.0004		.0011		.022
#3 Impinger$^{(d)}$										2165.								
Run 56	Electrostatic precipitator outlet stream																	
Probe																		
dry material		8.7		Trace	0.004	0.035	0.035	0.64	1.31	1.45		0.14	0.14	0.025	0.004	0.014	0.004	1.94
H_2O wash		12.4		<.0007	<.0004	0.212	0.071	0.14	0.14	1.87		0.071	0.35	0.001	<.001	0.004	0.007	0.14
organic wash																		
Total Probe		21.1			0.004	0.247	0.106	0.78	1.45	3.32		0.211	0.49	0.026	0.004	0.018	0.011	2.08
Filter		20.4	Trace	<.0004	0.018	0.18	0.35	1.34		3.04		0.21	1.52	0.071	<.004	0.011	0.011	2.47
Impingers																		
#1 H_2O wash				<.00004	0.011	<.002	0.002	0.001	0.011	27.5	(4.8)	0.0007	0.004	<.0004	<.002	<.0004	<.0002	0.0004
#1 organic wash				<.00004	.001	.004	.0004	.0007	.014	0.42		.0007	.007	.0007	<.002	.0003	<.0002	.011
#2 H_2O wash				<.00004	.0004	<.002	.0007	.001	.003	37.8		.0007	.004	<.0004	<.002	<.0004	<.0002	.0007
#2 organic wash				<.00004	.004	.007	.002	.004	.011	0.28		.003	.007	<.0004	<.002	.0003	<.0002	.007
Total for #1 and #2					.016	.011	.0051	.0067	.039	66.0		.005	.022	.0007	<.002	.0006	<.0002	.019
#3 Impinger$^{(d)}$										2055								

TABLE 14C. DISTRIBUTION OF CHEMICAL ELEMENTS AMONG THE PORTION OF PARTICULATE CATCH WITH A SINGLE FILTER ARRANGEMENT[a] (Cont'd)

Run and Sample Portion[b]	Elemental Analysis,[d] mg/m^3 (Cont'd)															
	Ni	Co	Cu	As	Sr	Zr	Mo	Ag	Cd	Sn	Sb	Ba	Hg	Pb	Totals	Totals[f] minus Sulfur
Run 55 (Cont'd)																
Probe																
dry material	0.99	0.11	0.67	<0.35	0.32	0.67	0.071	<.18	<.35	<.35	<.35	1.66	<.011	0.32	1308.	1183.
H_2O wash	<.004	<.002	0.071	<0.04	<.04	<.004	<.004	<.004	<.04	<.02	<.02	0.007		0.021	19.9	4.5
organic wash	<.001	<.001	<.0001	<0.001	<.01	<.001	<.001	<.0001	<.001	<.007	<.007	<.001		<.007	0.004	0.004
Total Probe	0.99	0.11	0.74		0.32	0.67	0.071					1.67		0.34	1327.9	1187.5
Filter	0.14	0.025	<.071	1.31	0.25	<.035	0.035	<.014	<.014	<.071	<.071	0.032	0.011	<.011	195.8	168.4
Impinger																
#1 H_2O wash		<.004	0.0007	<.004	<.004	<.004	<.004	<.00004	<.0018	<.0018	<.0018	<.00004		<.0018	88.3	0.029
#1 organic wash		<.004	<.00004	<.004	<.004	<.004	<.004	<.00004				<.00004		<.0018	0.022	0.023
#2 H_2O wash		<.004	0.0004	<.004	<.004	<.004	<.004	<.00004				<.00004		<.0018	208.4	0.017
#2 organic wash		<.004	0.0011	<.004	<.004	<.004	<.004	<.00004				<.0004		<.0018	1.04	0.087
Total for #1 and #2			0.0022						<.0018	<.0018	<.0018				297.7	0.156
#3 Impinger[g]															2165.	
Run 56 (Cont'd)																
Probe																
dry material	0.011	<.001	0.14	0.001	0.001	0.001	0.001	0.007	<.014	<.001	<.003	0.007		0.001	5.9	4.46
H_2O wash	0.071	<.001	0.14	<.014	<.014	<.001	<.001	0.0004	<.014	0.007	<.007	0.004		0.007	3.2	1.37
organic wash																
Total Probe	0.082		0.28	0.001	0.001	0.001	0.001	0.0074		0.007		0.011		0.008	9.1	5.83
Filter	0.011	<.004	<.035	0.035	0.071	Trace	<.004	Trace	<.004	0.11	<.025	0.003		0.035	9.6	6.45
Impingers																
#1 H_2O wash		<.002	0.0001	<.002	<.002	<.002	<.002	<.00004	<.001	<0.0002	<.001	0.0002		<.001	27.6	0.030
#1 organic wash		<.002	0.0007	<.002	<.002	<.002	<.002	<.00004	<.001	0.002	<.001	0.004		<.001	0.47	0.046
#2 H_2O wash		<.002	0.0003	<.002	<.002	<.002	<.002	<.00004	<.001		<.001	<.0002		<.001	37.8	0.011
#2 organic wash		<.002	0.00004	<.002	<.002	<.002	<.002	<.00004	<.001		<.001	0.0002		<.001	0.33	0.046
Total for #1 and #2			0.0011							0.002		0.0044			66.2	0.133
#3 Impinger[g]															2055.	

FOOTNOTES FOR TABLES 14A, 14B, AND 14C

(a) Runs 49-50 and 55-56 are pairs of runs collected during simultaneous sampling at the electrostatic precipitator inlet and outlet at the Edgewater Power Station, Lorain, Ohio.

(b) The headings dry material, H_2O wash, and organic wash used in this column refer to the dry portion, water portion, and acetone-methylene chloride portion of the catch, respectively.

(c) This sample was collected simultaneously with the particulate sample but by a separate train connected to an adjacent port in the duct. Although isokinetic conditions were not attempted for this train, the quartz wool plug used to filter particulate from the gas sample was analyzed for total sulfur and has been included in the total sulfur catch reported in this column.

(d) The elements were determined largely by OES analysis with confirmatory analyses and S analyses by XRF. The symbol < indicates that the element was sought but not detected in an anlysis having a detection limit as shown for the aliquot used. In some impinger samples, two values are shown for sulfur: the first and larger number represents total sulfur, the second represents sulfate sulfur.

(e) The total catch without sulfur included is intended to show the distribution of the total catch of element cations of the particulate among the portions of the rig and facilitate comparison of Electrostatic Precipitator and outlet streams.

(f) Glassware connecting the first and second filters.

(g) The #3 impinger contained 100 ml of 6 to 7 percent H_2O_2 in water for oxidation of SO_2 remaining in the gas stream. The efficiency of this single oxidation impinger is untested but, from the performance of the first bubbler in the Goksøyr-Ross procedure, is anticipated to be good.

and 52) total sulfur determinations were obtained on all subsamples and sulfate sulfur was determined if the amount of total sulfur was sufficient to warrant it.

Except for a confirming elemental analyses on three quartz filter deposits by X-ray emission spectroscopy (XRF), all metallic determinations on filters and solutions were obtained by optical emission spectroscopy (OES) techniques. Only three filters were analyzed by XRF because sample amounts were not sufficient to be related quantitatively to previously prepared standards. The major elements were determined by OES after dilution of the sample to adjust the elemental concentrations of the samples to correspond to elemental concentration of available standards. The data obtained on the three filter samples by XRF and OES agree within the limits of accuracies of the two methods. Low amounts of metals found in the wash solutions indicated XRF analyses would not be useful.

Probe and impinger washes were treated according to the sulfur analyses desired. For measuring the total sulfur of water washes, an appropriate portion of the sample was made basic with NaOH to convert all species of sulfur to the stable sodium salts. For the determination of sulfur which was collected as a sulfate, the other portion of the sample was treated with HCl to retain only the sulfate sulfur. Both portions were subjected to XRF analyses for sulfur content.

For the organic wash solutions, where only total sulfur content was obtained, the mixture of methylene chloride and acetone was digested and measured for sulfur by XRF or a wet chemical method.

Figure 20 shows an analytical route outline followed in characterizing the emission collection runs.

Table 15 shows a more definitive breakdown of sample forms, treatment, preparation, and corresponding analyses when referred to the accompanying legends. These include Hg analyses of the probe and impinger water washes and some sulfur checks using wet chemistry.

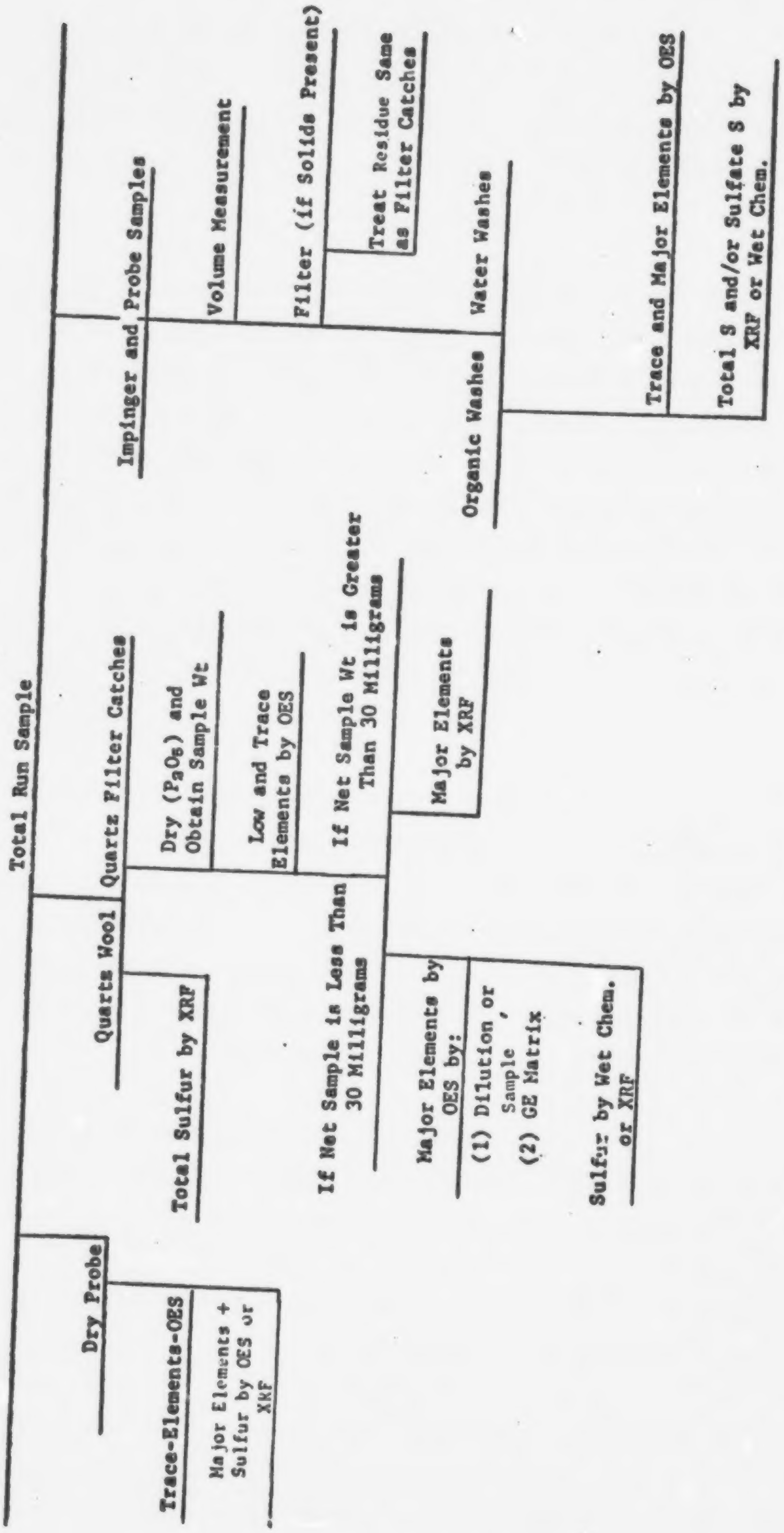

Total Run Sample
Dry Probe
Trace-Elements-OES
Major Elements + Sulfur by OES or XRF
Quartz Wool
Total Sulfur by XRF
Quartz Filter Catches
Dry (P_2O_5) and Obtain Sample Wt
Low and Trace Elements by OES
If Net Sample is Less Than 30 Milligrams
Major Elements by OES by:
(1) Dilution or Sample
(2) GE Matrix
Sulfur by Wet Chem. or XRF
If Net Sample Wt is Greater Than 30 Milligrams
Major Elements by XRF
Impinger and Probe Samples
Volume Measurement
Filter (if Solids Present)
Treat Residue Same as Filter Catches
Water Washes
Organic Washes
Trace and Major Elements by OES
Total S and/or Sulfate S by XRF or Wet Chem.

FIGURE 20. FLOW SHEET FOR PROCEDURES IN TREATMENT AND ANALYSES OF STACK EMISSION SAMPLES

TABLE 15. GENERAL SAMPLE DESCRIPTIONS, TREATMENTS, AND ANALYTICAL METHODS FOR CHARACTERIZATION OF STACK SAMPLES TAKEN AT EDGEWATER POWER PLANT, LORAIN, OHIO

Sample Description			Preliminary Sample Treatment	Desired Analysis	Additional Sample Treatment	Analytical Method and Technique	Desired Analysis	Additional Sample Treatment	Analytical Method and Technique	Desired Analysis	Additional Sample Treatment	Analytical Method and Technique
Run(s)	Sample Location	Sample Form										
44, 49, 50, 55, 56	Quartz Filter 1	Solid Deposit	1A1, 1B2	2A, B, C	1CE, D	3-A1a, c	2B, E	1D, G	3-B1a			
49, 50	Quartz Filter 2	Solid Deposit	1A1, 1B2	2A, B, C	1CE, D	3-A1a, c	2B, E	1D, G	3-B1a			
46, 47, 48, 51, 52	Quartz Filter 1	Solid Deposit	1A1, 1B2	2A, B, C	1CE, D	3-A1a, c	2E	1D, G	3-B1a	2F	1C, H1, G	3-B1a
52	Quartz Filter 2	Solid Deposit	1A1, 1B2	2A, B, C	1CE, D	3-A1a, c	2E	1D, G	3-B1a	2F	1C, H1, G	3-B1a
49, 55, 36	Probe	Loose Powder	1B2	2A, B, C	1D, M	3-A2	2E	1D, G	3-B1a			
46, 47, 48, 51, 52	Probe	Loose Powder	1B2	2A, B, C	1D, M	3-A2	2E	1D, G	3-B1a			
44, 49, 50, 55, 56	Probe Wash H_2O	Liquid & Solid	1F	-			-					
44, 49, 50, 55, 56	Probe Wash H_2O	Liquid	1K	2A, B, C	1DA2	3-A1b	2E	1I	3-B2			
44, 49, 50, 55, 56	Probe Wash H_2O	Solid	1B2	-			-					
46, 47, 48, 51	Probe Wash H_2O	Liquid & Solid	1F	-			-					
46, 47, 48, 51, 52	Probe Wash H_2O	Liquid	1K	2E	1C1	3-B2	2F	1CH2	3-B2			
46, 47, 48, 51	Probe Wash H_2O	Solid	1B2	-			-					
49, 50	Probe Wash Organic	Liquid & Solid	1F	-			-					
49, 50, 44, 55, 56	Probe Wash Organic	Liquid	1K	2A, B, C	1DA2	3-A1b	2E	1J	3-C			
49, 50	Probe Wash Organic	Solid	1B2	-			-					
46, 47, 48, 51, 52	Probe Wash Organic	Liquid	1K	2E	1-J	3-B2	-					
44, 49, 50, 55, 56	Impinger Wash-H_2O #1 & 2	Liquid	1K	2A, B, C	1-DA2	3-A1b	2E	1CI	3-B2	2F	1CH2	3-B2
46, 47, 48, 51, 52	Impinger Wash-H_2O #1 & 2	Liquid	1K	2E	1CI	3-B2	2F	1CH2	3-B2			
46, 47	Impinger Wash-H_2O #3 & 4	Liquid	1K	2E	1CI	3-B2	2F	1CH2	3-B2			
48	Impinger Wash-H_2O #3	Liquid & Solid	1F	-	-	-	-	-	-			
48	Impinger Wash-H_2O #3	Liquid	1K	2E	-	-	2F	-	-			
48	Impinger Wash-H_2O #3	Solid	1B2	-	-	-	-	-	-			
48	Impinger Wash-H_2O #4	Liquid	1K	2E	-	-	2F	-	-			
46, 47, 48	Impinger Wash-H_2O Aliquot #1 & 2	Liquid	1K	2E	-	-	2F	-	-			
46, 47	Impinger Wash-H_2O Aliquot #3 & 4	Liquid	1K	2E	-	-	2F	-	-			
48	Impinger Wash-H_2O Aliquot #3	Liquid & Solid	1F	-	-	-	-	-	-			
48	Impinger Wash-H_2O Aliquot #3	Liquid	1K	2E	-	-	2F	-	-			
48	Impinger Wash-H_2O Aliquot #3	Solid	1B2	-	-	-	-	-	-			
48	Impinger Wash-H_2O Aliquot #4	Liquid	1K	2E	-	-	2F	-	-			
44, 49, 50, 55, 56	Impinger Wash Organic #1 & 2	Liquid	1K	2A, B, C	1DA2	3-A1b	2E	1CI	3-B2			
46, 47, 48, 51, 52	Impinger Wash Organic #1 - 4	Liquid	1K	2E	1J	3-B2	-					
44, 49, 50, 55, 56	Quartz Wool	Solid Deposit	1B1	2E	1DG	3-B1b	-					
53, 54, (46-47-48) (51-52)	Quartz Wool	Solid Deposit	1B1	2E	1DG	3-B1b						

TABLE 15. (Cont'd)

Sample Description Run(s)	Sample Location	Sample Form	Preliminary Sample Treatment	Desired Analysis	Additional Sample Treatment	Analytical Method and Technique	Desired Analysis	Additional Sample Treatment	Analytical Method and Technique	Desired Analysis	Additional Sample Treatment	Analytical Method and Technique
44, 49, 50, 55, 56	Quartz Filter 1	Solid Deposit	1A1, 1B2	2A, B, C	1CE, D	3-A1a, e	2B, E	1D, G	3-B1a			
49, 50	Quartz Filter 2	Solid Deposit	1A1, 1B2	2A, B, C	1CE, D	3-A1a, e	2B, E	1D, G	3-B1a			
46, 47, 48, 51, 52	Quartz Filter 1	Solid Deposit	1A1, 1B2	2A, B, C	1CE, D	3-A1a, e	2E	1D, G	3-B1a	2F	1C, H1, G	3-B1a
52	Quartz Filter 2	Solid Deposit	1A1, 1B2	2A, B, C	1CE, D	3-A1a, e	2E	1D, G	3-B1a	2F	1C, H1, G	3-B1a
49, 55, 56	Probe	Loose Powder	1B2	2A, B, C	1D, M	3-A2	2E	1D, G	3-B1a			
46, 47, 48, 51, 52	Probe	Loose Powder	1B2	2A, B, C	1D, M	3-A2	2E	1D, G	3-B1a			
44, 49, 50, 55, 56	Probe Wash H_2O	Liquid & Solid	1F	-			-					
44, 49, 50, 55, 56	Probe Wash H_2O	Liquid	1K	2A, B, C	1DA2	3-A1b	2E	1I	3-B2			
44, 49, 50, 55, 56	Probe Wash H_2O	Solid	1B2	-			-					
46, 47, 48, 51	Probe Wash H_2O	Liquid & Solid	1F	-			-					
46, 47, 48, 51, 52	Probe Wash H_2O	Liquid	1K	2E	1C1	3-B2	2F	1CH2	3-B2			
46, 47, 48, 51	Probe Wash H_2O	Solid	1B2	-			-					
49, 50	Probe Wash Organic	Liquid & Solid	1F	-			-					
49, 50, 44, 55, 56	Probe Wash Organic	Liquid	1K	2A, B, C	1DA2	3-A1b	2E	1J	3-C			
49, 50	Probe Wash Organic	Solid	1B2	-			-					
46, 47, 48, 51, 52	Probe Wash Organic	Liquid	1K	2E	1-J	3-B2	-					
44, 49, 50, 55, 56	Impinger Wash-H_2O #1 & 2	Liquid	1K	2A, B, C	1-DA2	3-A1b	2E	1CI	3-B2	2F	1CH2	3-B2
46, 47, 48, 51, 52	Impinger Wash-H_2O #1 & 2	Liquid	1K	2E	1CI	3-B2	2F	1CH2	3-B2			
46, 47.	Impinger Wash-H_2O #3 & 4	Liquid	1K	2E	1CI	3-B2	2F	1CH2	3-B2			
48	Impinger Wash-H_2O #3	Liquid & Solid	1F	-	-	-	-	-	-			
48	Impinger Wash-H_2O #3	Liquid	1K	2E	-	-	2F	-	-			
48	Impinger Wash-H_2O #3	Solid	1B2	-	-	-	-	-	-			
48	Impinger Wash-H_2O #4	Liquid	1K	2E	-	-	2F	-	-			
46, 47, 48	Impinger Wash-H_2O Aliquot #1 & 2	Liquid	1K	2E	-	-	2F	-	-			
46, 47	Impinger Wash-H_2O Aliquot #3 & 4	Liquid	1K	2E	-	-	2F	-	-			
48	Impinger Wash-H_2O Aliquot #3	Liquid & Solid	1F	-	-	-	-	-	-			
48	Impinger Wash-H_2O Aliquot #3	Liquid	1K	2E	-	-	2F	-	-			
48	Impinger Wash-H_2O Aliquot #3	Solid	1B2	-	-	-	-	-	-			
48	Impinger Wash-H_2O Aliquot #4	Liquid	1K	2E	-	-	2F	-	-			
44, 49, 50, 55, 56	Impinger Wash Organic #1 & 2	Liquid	1K	2A, B, C	1DA2	3-A1b	2E	1CI	3-B2			
46, 47, 48, 51, 52	Impinger Wash Organic #1 - 4	Liquid	1K	2E	1J	3-B2	-					
44, 49, 50, 55, 56	Quartz Wool	Solid Deposit	1B1	2E	1DG	3-B1b	-					
53, 54, (46-47-48) (51-52)	Quartz Wool	Solid Deposit	1B1	2E	1DG	3-B1b						

FOOTNOTES FOR TABLE 15

1. Sample Treatment Legend for Table 15.
   - A. Drying
     - 1. In the presence of P_2O_5
     - 2. A 10 ml aliquot of solution on graphite
   - B. Weighings
     - 1. Gross (residue plus filter)
     - 2. Net (residue)
   - C. One-half of sample
   - D. Aliquot (considerably less than half of the sample)
   - E. Pulverize and mix filter and residue in shaker
   - F. Sediments of washings filtered onto quartz filters
   - G. Mix with quartz matrix and briquette to form solid disk
   - H. Treat with HCl for determination of sulfur as sulfate
     - 1. Filter samples: place one-half of filter specimen in an alumina crucible, fill with 1:1 $HCl:H_2O$ solution, heat to dryness
     - 2. Water wash solutions: place about one-half of the total solution in a beaker, add about 20 ml of 1:1 $HCl:H_2O$ for each 100 ml of sample, boil for 1 hour
   - I. Make water solutions basic with NaOH to convert all lower sulfur oxides to stable sodium salts
   - J. Total sulfur determinations in organic washes; add 10 ml of bromine water and 40 ml of 1:1 nitric acid:water to the beaker containing the total organic wash solution; let the mixture stand at room temperature for about 1/2 hour; heat slightly with care until the methylene chloride has vaporized, and the nitric acid has digested the acetone; concentrate the remaining aqueous solution
   - K. Volume measurement
   - L. Diluted with germanium to cover major elements.

2. Desired Analyses Legend for Table 15.
   - A. Semiquantitative for the elements
   - B. Quantitative analysis for the elements
   - C. Trace elements (Cd, Be, Pb, As, and Hg)
   - D. Hg
   - E. Total sulfur content
   - F. Sulfate sulfur content.

3. Analytical Method Legend for Table 15.
   - A. Optical emission spectroscopy (OES)
     - 1. Semiquantitative analyses for metals
       - a. Quartz standards (range--0.01 to 0.3%, sample weight--10 mg, expected accuracy -- ± 50%).
         Note: procedure not applicable for Hg analyses.

FOOTNOTES FOR TABLE 15 (Cont'd)

   - b. Carbon Standards (conditions above apply)
   - c. For Hg analyses--using the same standards as above except that a small orificed cap is used (Boiler Cap Technique)
  2. Quantitative analyses for metals--Germanium matrix technique (range--0.01 to 10.%; sample weight ratios; 10 mg of sample, 90 milligrams of Ge, and 100 mg of graphite; expected accuracy-- ± 20%)

B. X-ray emission spectroscopy (XRF)
  1. Solids
     - a. Quantitative analyses of major elements using quartz standards and pressed disks; detectable range--0.05 to 10. mg; sample weight ratios--25 mg of actual residue sample, 175 mg of quartz, and 50 mg of pressable graphite x; expected accuracy ± 5%

     - b. Estimation of sulfur content in pressed samples of quartz matrix where sample weights are either too small for normal sample weight ratios or where the weight of the actual sample cannot be determined
  2. Solutions quantitative analyses of sulfur in wash solutions, either water or converted organic. Range--0.05 to 5.0 mg per ml of solution; expected accuracy--±10%.

C. Wet (classical chemistry)
  1. Quantitative analyses for total sulfur, as used on some wash solutions; determined gravimetrically after precipitating as barium sulfate.

IV. DISCUSSION OF RESULTS

- OVERALL COMPOSITIONS AND MATERIAL BALANCES
- SAMPLING APPARATUS AND PROCEDURES
    - Probe
    - Filter
    - Impinger
  - Sampling Train Modifications
    - Simultaneous Sampling
    - Use of the G/R Coil in Particulate Sampling
    - Field Trials
  - Sample Handling
  - Suggested Sampling Procedures
  - Inorganic Ash (less S)
  - Sulfur Compounds

IV. DISCUSSION OF RESULTS

The results of several sets of experiments reported earlier have been brought together so as to reveal overall patterns of mass distribution in the train. The discussion of these patterns and their significances has been subdivided into separate topics under the headings:

(1) Material balances and overall composition
(2) Sampling apparatus and procedures
(3) Inorganic ash (less S)
(4) Sulfur compounds.

OVERALL COMPOSITIONS AND MATERIAL BALANCES

Material balances have been made in an attempt to account for all of the mass of material collected in the various research samples. These material balances were used to evaluate the effects of sampling-train modifications on particulate catch, to identify the extent to which the various chemical species are controlled, and to estimate the apparent overall efficiency of collection.

Because of the difficulties in obtaining reproducible operation and sampling conditions, a considerable amount of uncertainty usually exists in interpretation of the results from the sampling of particulate in stack gases. The changes in particulate composition and mass that occur during sampling and analysis are reflected in the material and lend further uncertainties to the interpretation. For these reasons, such material balances have been attempted at several stages in the collection of experimental data. This portion of the report summarizes the results of those trial material balances and includes the conclusions that can be drawn concerning the nature and distribution of the catch.

The degree of success that has been possible in accounting for the total mass of a group of particulate samples is illustrated by Table 16 for coal-burning operation of the Battelle Multifuel Furnace. For that furnace, the flue-gas line from which the sample was withdrawn was

TABLE 16. DERIVED QUANTITIES AND TRIAL MATERIAL BALANCES

Description (a)	Sampling Mode (a)	Run and Portion (b)		Estimated Product Components, mg							Totals as		Material Balance, Percent (k)	Gas Sampled, m^3	Concentrations			Distribution		
				XRF Oxides (c)	Other Oxides (d)	SiO_2 (e)	H_2SO_4 (f)	C (g)	H_2O (h)	N_2O_5 (i)	Sum	Collected (j)			Sum, mg/m^3	H_2SO_4, mg/m^3	Ash, mg/m^3 (l)	Sum, Percent (m)	H_2SO_4, Percent (n)	Ash, (o)
Quartz filter at 280 F	F	9	P	37	5	17	87	8	36	1	191	186	103					38	32	37
			F	55	8	23	122	1	--	-	209	202	103					41	45	54
			I	12	2	--	60	13	17	3	107	101	106					21	22	9
			T	104	15	40	269	22	53	4	507	489	104	0.463	1090	581	343	100	100	100
Quartz filter at 280 F	F	24	P	75	10	36	42	7	--	-	170	189	90					39	36	44
			F	92	13	47	47	1	14	-	214	190	112					46	41	55
			I	2	--	--	27	2	30	3	64	35	183					15	23	1
			T	169	23	83	116	10	44	3	448	414	108	0.327	1370	355	841	100	100	100
Quartz filter at 400 F	G	10	P	471	66	220	82	3	27	-	869	990	88					61	36	71
			F	150	21	79	19	1	4	-	274	282	97					19	8	24
			I	33	5	10	127	4	102	1	281	533	53					20	56	5
			T	654	92	309	228	8	133	1	1424	1805	79	0.516	2760	441	2040	100	100	100
Quartz filter at 400 F	G	26	P	180	25	71	30	18	--	-	324	418	78					57	40	72
			F	55	8	40	19	4	3	-	129	202	64					22	24	27
			I	2	--	1	27	2	83	2	117	142	81					21	36	1
			T	237	33	112	76	24	86	2	570	768	74	0.406	1410	188	940	100	100	100
Inconel probe and quartz filter at 230 F	B	13	P	136	19	84	98	5	--	1	343	567	61					51	51	59
			F	100	14	53	74	-	33	-	274	235	116					36	38	41
			I	2	--	--	22	12	50	2	83	77	114					13	11	--
			T	238	33	137	194	17	83	3	705	879	80	0.392	1800	495	1040	100	100	100
Stainless steel probe and quartz filter at 230 F	A	14	P	192	27	80	115	3	7	-	424	501	85					55	41	66
			F	94	13	47	143	1	61	1	360	292	123					39	52	34
			I	2	--	--	20	7	16	3	48	74	65					6	7	--
			T	288	40	127	278	11	84	4	832	867	96	0.601	1390	463	756	100	100	100
Quartz probe and quartz filter at 230 F	C	15	P	49	7	22	75	2	22	1	178	203	88					38	45	43
			F	61	8	32	73	-	35	-	209	168	124					38	43	55
			I	2	-	1	21	4	79	2	109	133	82					24	12	2
			T	112	15	55	169	6	136	3	496	504	98	0.336	1480	504	541	100	100	100
Quartz probe and quartz filter at 230 F	C	23	P	93	13	42	60	35	--	-	243	358	68					42	35	50
			F	86	12	46	81	1	27	-	253	214	118					40	48	49
			I	2	--	--	28	2	70	2	104	87	119					18	17	1
			T	181	25	88	169	38	97	2	600	659	91	0.332	1810	509	885	100	100	100

TABLE 16. DERIVED QUANTITIES AND TRIAL MATERIAL BALANCES (Cont'd)

Description (a)	Sampling Mode (a)	Run and Portion (b)		Estimated Product Components, mg							Total as		Material Balance, Percent (k)	Gas Sampled, m^3	Concentrations			Distribution		
				XRF Oxides (c)	Other Oxides (d)	SiO_2 (e)	H_2SO_4 (f)	C (g)	H_2O (h)	N_2O_5 (i)	Sum	Collected			Sum, mg/m^3	H_2SO_4, mg/m^3	Ash, mg/m^3 (l)	Sum, Percent (m)	H_2SO_4, Percent (n)	Ash, (o)
Hot filter with coil after filter	H	17	P	44	6	18	28	2	1	1	100	130	77					32	38	33
			F	82	11	41	25	--	3	-	162	132	123					52	34	64
			I	5	1	--	21	12	8	3	50	43	116					16	28	3
			T	131	18	59	74	14	12	4	312	305	102	0.336	930	220	620	100	100	100
Hot filter with coil after filter	H	28	P	70	10	35	14	3	--	1	132	149	89					28	25	32
			F	143	20	75	20	9	2	1	270	274	99					58	36	66
			I	6	1	--	22	3	31	3	66	94	70					14	39	2
			T	219	31	110	56	15	33	5	469	517	91	0.310	1510	181	1160	100	100	100
Same as H, but 2x sampling time	I	18	P	32	4	21	36	7	1	1	102	116	88					32	32	33
			F	71	10	35	29	2	10	1	158	155	102					46	26	67
			I	1	--	--	47	9	10	5	72	194	37					22	42	--
			T	104	14	56	112	18	21	7	332	465	71	0.632	525	177	276	100	100	100
Same as H, but 2x sampling time	I	29	P	158	22	76	22	4	--	-	282	340	83					29	8	40
			F	163	23	80	18	1	6	-	291	311	94					29	7	42
			I	81	11	24	228	1	73	2	420	628	67					42	85	18
			T	402	56	180	268	6	79	2	993	1279	78	0.685	1450	392	933	100	100	100
Coil ahead of hot filter	K	19	P	19	3	8	67	2	31	1	131	131	100					40	38	48
			F	21	3	8	88	1	65	-	186	118	158					37	51	51
			I	1	-	--	19	4	46	3	73	70	104					23	11	1
			T	41	6	16	174	7	142	4	390	319	122	0.386	1010	451	163	100	100	100
Coil ahead of hot filter	K	31	P	162	23	89	116	6	--	-	396	409	97					72	63	87
			F	25	3	11	53	9	22	1	124	95	130					18	29	12
			I	2	--	--	14	2	38	2	58	60	97					10	8	1
			T	189	26	100	183	17	60	3	578	564	102	0.389	1490	470	810	100	100	100

FOOTNOTES FOR TABLE 16

(a) See Table 7.

(b) P = probe, F = filter, I = impinger, T = total.

(c) The sum of the elements analyzed by XRF x 1.54 = oxide equivalent, S excluded.

(d) The sum of the elements analyzed by OES but not by XRF expressed as oxides, approximate.

(e) Estimated by assuming Al and Si arise from clay minerals. Here assume Al:Si = 1.0 and convert the Si to the equivalent weight.

(f) Assuming all S is present as H_2SO_4.

(g) The carbon content found by combustion analysis.

(h) Based on the H content found by combustion. Reduce the total H by a weight equal to 1/12 of the carbon found as an estimate of organic H and multiply remainder by 9 to express as H_2O.

(i) The N content is expressed as N_2O_5.

(j) The mass of each catch portion as originally measured, see Table 8.

(k) $\frac{100 \times \text{sum}}{\text{as collected}}$ = percent.

(l) The sum of XRF oxides, other oxides, and SiO_2 as estimated expressed per m^3 gas sampled.

(m) Calculated from the sums for each portion but the filter catch is reduced by omitting the H_2O listed for that portion. Expressed as percent of the total catch (Sum).

(n) The distribution of H_2SO_4 as measured.

(o) The distribution of the sum of XRF oxides, other oxides and SiO_2 as estimated.

approximately 1 and 1/2 inch inside diameter and sample averaging by traversing was unnecessary and impractical. Some uncertainty arose due to the necessity for using an estimated value for the amount of SiO_2 in the inorganic portion of the catch on the quartz filter. The table shows that somewhat better consistency is found in the percentage distribution of a component of the catch among several portions than in the actual mass of that component found in comparable samples. Some samples show good material balance in all portions while others do not, mainly because of poor balance in both probe and impinger portions (see for example Runs 10, 18, 26, 28, and 29). This scatter is believed to result from the difficulties that arose during sample collection and in the taking of aliquots of sample residues for analysis. Later, field experiments showed oxidation and evaporation (see Table 13) of samples during the usual method of storage in partly filled bottles was a problem. Aliquots collected in the field and stored in completely filled bottles showed substantially less sulfate content compared to conventionally stored samples.

Using these material balances, the comparison of the material distributions for the pairs of runs representing the various sampling modes yield the following generalizations:

A. Modes F and G differ in filter temperature, and the use of the higher filter temperature in G caused a substantially higher fraction of the sulfur to be collected in the impinger.

B. Modes C and F differ in probe temperature, and, in these runs where substantial portions of the catch are found in the probe, no clear effect of the temperature change is identifiable.

C. Modes C and G differ in both probe and filter temperatures, and again a substantially higher fraction of the S is found in the impinger for the runs (Mode G) with the higher filter (and probe) temperature.

D. Modes H and G differ in that a coil was used to collect H_2SO_4 between filter and impinger in Mode H. Any difference in SO_2 retention that may have thus resulted in the impinger portions is masked by considerable scatter of the data.

E. Modes H and I differ in sampling time and amount of gas sampled since the intended half-flow rate for Mode I was not used. Only one run in Mode I showed the expected large particulate collection and, in that case, substantial breakthrough of ash and S into the impinger is indicated.

F. Modes H and K differ in use of a coil before the filter to collect H_2SO_4 and in this case the additional H_2SO_4 retention has an effect similar to the use of a cooler filter temperature in that the S collection in the impinger is reduced.

Differences in total S catch for these two modes suggests substantial differences in furnace performance on two separate days. These differences in total S make difficult any determination of the effect of the coil on the filter catch.

An important observation arising from these trial balances was the apparent presence of a substantial amount of water in the catch for some portions. Following evaporation and desiccation of the several portions of a catch from the coal-fired laboratory furnace, aliquots were taken for C, H, and N analyses. The results were presented as part of Table 8 and are repeated here as Table 17. These aliquots generally showed greater H content than could be accounted for by any assumption of organic structure using the analytical value for the carbon content. Accordingly, the excess H was estimated as H_2O and included as such in the material balance in Table 16. This inclusion of H_2O in the balance generally improved the balance for the probe and impinger portions which had been collected as residues from water solution. On the other hand, the inclusion of such water in the material balance for the filter portion apparently is incorrect. The handling of filter portions had consisted mainly of prolonged storage over Drierite, followed by grinding and collection of aliquots, and, in spite of a re-desiccation of these aliquots, an appreciable amount of water was found in these filter samples by C, H, N analyses. Table 16 shows that this water content consistently caused the filter catch material balance to total over 100 percent, but these balances were usually close if the water was excluded. Accordingly, this water content is believed

TABLE 17. SUMMARY OF C-H-N ANALYSES FOR PARTICULATE SAMPLES (Multifuel Furnace Facility, see Table 8)

		Portion[a], weight percent			
Run	Element	P	F	I	T
9	C	8.0	1.0	13.2	22.2
	H	4.7	nil	3.0	7.7
	N	0.4	0.1	0.9	1.4
10	C	2.9	0.5	4.0	7.4
	H	3.2	0.5	11.7	15.4
	N	—	0.1	0.2	0.3
11	C	17.7	7.2	3.0	27.9
	H	—	5.3	8.9	14.2
	N	0.4	0.3	3.9	4.6
10	C	9.2	(b)	7.2	(b)
	H	2.4	(b)	8.1	(b)
	N	0.2	(b)	0.5	(b)
13	C	4.7	0.4	12.0	17.1
	H	—	3.7	6.6	10.3
	N	0.2	0.1	0.7	1.0
14	C	2.9	0.8	7.0	10.7
	H	1.0	6.9	2.3	10.2
	N	0.1	0.3	1.0	1.4
15	C	1.6	0.3	4.3	6.2
	H	2.6	3.9	9.1	15.6
	N	0.2	0.1	0.6	0.9
17	C	2.4	0.4	11.9	14.7
	H	0.3	0.4	1.9	2.6
	N	0.2	—	1.0	1.2
18	C	7.0	1.7	8.9	17.6
	H	0.6	1.3	11.6	13.5
	N	0.4	0.3	1.4	2.1
19	C	1.8	0.5	3.9	6.2
	H	3.5	7.2	5.4	16.2
	N	0.3	0.1	1.1	1.5
23	C	34.7	1.0	2.2	37.9
	H	1.3	3.1	8.0	12.4
	N	—	0.1	0.6	0.7

(a) The letters in this row are column headings -

P = Probe
F = Filter
I = Impinger
T = Total.

(b) The glass filter used for this sample is not suitable for the C-H-N analysis train.

to be an artifact of sample handling and not part of the original catch. The subsequent investigation of desiccation properties of probe and impinger samples from the cyclone-fired boiler at the Niles, Ohio, plant of Ohio Edison Company (see Table 11) confirms that some portions are difficult to dry, especially those that include free sulfuric acid.

Trial balances from some samples collected from the pulverized coal-fired boilers at the Edgewater Power Station, Lorain, Ohio, are possible using the data of Table 12. These support the conclusion that was reached for samples from the Multifuel Furnace, that the analyses of the impingers usually show greater SO_3 content and less total sulfur than found by the G/R procedure. The differences between the G/R impinger analyses are consistent with the anticipated volatilization losses for impinger samples and with the experimental demonstrations that SO_3 is apparently being generated by oxidation of the substantial amounts of SO_2 retained in the impinger.

The material balances for the particulate samples collected from the large pulverized coal-fired boilers are shown in Table 18. The weights of metal oxides and sulfuric acid shown in this table are derived from the analytical determinations of individual elements presented in Tables 14B and 14C. Inspection of that data had indicated that the trial balances would not account for substantial portions of the total catch. As the dry probe portion represented the major portion of the total catches, analyses to correct the major discrepancies in the trial balances were directed at those portions. C, H, N analyses were obtained on the dry probe portions of the catch to determine whether the inclusion of carbon contents (coke) would give a better material balance. These analyses, listed in Table 19, were used to derive the carbon contents listed in the material balances. For the material balances, the carbon contents of the filters were assumed to be about the same as those of the associated probe portions.

TABLE 18. TRIAL MATERIAL BALANCES FOR PARTICULATE SAMPLES FROM EDGEWATER POWER PLANT, LORAIN, OHIO

Run	Portion (a)	Sampling Location	mg/m^3 Metal Oxides (b)	mg/m^3 Estimated SiO_2 (c)	mg/m^3 SO_2 (d)	mg/m^3 C (e)	mg/m^3 Sum (f)	mg/m^3 Collection (f)	Material Balance, Percent	Distribution, Percent Sum	Distribution, Percent SO_2(d)	Distribution, Percent Oxides
49	P	E.P. inlet	2174		200	501	2875	3093	93	57	36	56.9
	F		638	1010	74	(152)(h)	1874	1597	117	37	13	43.1
	I		0.23		282		282	(g)	(g)	6	51	0
	T		2812	1010	556	(653)(h)	5031	(g)	101(i)	100	100	100
50	P	E.P. outlet	0.76		4.1		4.9	37.4	13	1.6	1.5	2.2
	F		33.4		53		86.4	102.0	85	28.5	19.7	97.5
	I		0.12		212		212	(g)	(g)	70	78.8	0.3
	T		34.28		269		303	(g)	66(i)	100	100	100
55	P	E.P. inlet	1841		275	218	2334	3482	61	67	30	79.3
	F		261	220	54	(37)(h)	572	614	87	16	6	20.7
	I		0.25		595		595	(g)	(g)	17	64	0
	T		2102	220	924	(255)(h)	3501	(g)	71(i)	100	100	100
56	P	E.P. outlet	9.3		6.6		15.9	21.1	76	9.5	4.5	38.2
	F		9.5	5.4	6.1		21.0	20.4	102	12.5	4.2	60.8
	I		0.24		132		132	(g)	(g)	78	91.3	1.0
	T		19.0	5.4	145		169	(g)	89(i)	100	100	100

FOOTNOTES FOR TABLE 18

(a) The letters in this column represent
P = Probe
F = Filter
I = Impinger
T = Total.

(b) Oxides were calculated from the normal stoichiometry for each element that was detected. This figure represents the sum of these calculations, but omitting sulfur oxides. Si could not be determined on filter samples and is estimated separately, see (c).

(c) For the filter samples, SiO_2 was estimated from the Si content of the accompanying probe catch.

(d) All sulfur found is expressed here as SO_2; this includes dissolved SO_2 as collected.

(e) From the C, H, N analyses of Table 5.

(f) Sum represents the total of the estimates of oxides, H_2SO_4, and C. The column titled Collection, represents the mass of the catch obtained experimentally.

(g) The impinger solutions were analyzed as collected so that no estimates of residue remaining after evaporation were obtained.

(h) Based on the C analysis of the accompanying probe sample for the same experiment.

(i) Based on sum of probe and filter catch values only.

TABLE 19. CARBON, HYDROGEN, AND NITROGEN ANALYSES OF DRY PROBE MATERIALS, SAMPLES FROM EDGEWATER POWER STATION

	Weight, percent		
Run	C	H	N
49	16.6	0.1	0.1
55	8.8	0.1	<0.1
46	31.3	0.6	0.3
47	7.0	0.4	0.1
48	37.9	0.3	0.3
51	20.1	0.2	0.1
52	30.0	0.2	0.2

As for the data shown in Table 16, the trial balances of Table 18 reveal substantial separation of the component classes of the overall particulate in the sampling train. This fact, and the special difficulties associated with efficient collection of each component class, leads to the conclusion that the total catch is not conveniently nor accurately represented by a single number. Rather, expression of the total catch in terms of the amounts of the important individual chemical categories would permit the total to be judged on the basis of the level of emission for each material type. At present, total catch may include a summation of several distinct material categories with different chemistry and physical form

(1) Fly ash: solid particulate partially reacted with other ingredients of the stack gas

(2) Sulfur: present as free sulfuric acid, dissolved SO_2, and combined as sulfate and sulfite

(3) Organic material: condensates probably ranging from volatile materials to high-molecular weight materials such as benzpyrenes and metal-organic complexes

(4) Water: combined as hydrate water in the inorganic catch and water retained by the free sulfuric acid.

In summary, the conclusions from these trial material balances are:

(1) The assignment of definite oxide compositions to each of the elements (found analytically) makes possible trial material balances and these balances show substantial deviation from 100 percent in some cases. The uncertainties reflected by these trial balances represent uncertainties that arise from sampling and sample-handling procedures as much as from the inherent analytical difficulties.

(2) The inorganic ash portion is distributed differently among probe, filter, and impinger than is the sulfuric oxide portion. In the runs made using the Battelle Multifuel Furnace, less than 2 percent of the ash was found by chemical analysis in the impinger, whereas between 6 and 85 percent of the sulfur oxide catch was found there. Other results obtained from samples collected at Edgewater Power Station show substantially smaller percentages of ash in the impingers. Thus, the mass distribution of the catch usually does not correspond to the distribution of any single component of the particulate.

(3) The composition of the total catch varies too much to permit calculation of meaningful averages, but typical compositions for coal-burning operation based on these trial applications of the EPA train and its modifications would be:

	Battelle Multifuel Furnace Precipitator Inlet[a]	Edgewater Power Station Precipitator Inlet	Edgewater Power Station Precipitator Exhaust
Inorganic ash (less sulfur), wt percent	66	72	37
Sulfur, as H_2SO_4, wt percent	31	12 to 18	63
Carbon (coke of organics), wt percent	3	9 to 17	Not determined

(a) Average for all runs, dry basis.

(4) The total mass of elements found by chemical analysis, excluding sulfur, indicates that the precipitator at Edgewater Power Station removed 99 percent or better of the relatively coarse material caught in the probe and cyclone and at least 95 percent of the filter-catch portion. These two portions constitute about 99 percent of the total metal oxide catch as determined by analysis of both inlet and outlet streams. On a mass basis, the importance of the impinger catch arises from the large mass of sulfur compounds retained and from the possibility that some heavy metals present in low concentrations may be retained by the scrubbing action of the impinger. However, it seems probable that capture of both sulfur and heavy metals, if desired, can be accomplished better in other ways.

SAMPLING APPARATUS AND PROCEDURES

The major problems associated with the sampling and measurement of particulate emissions, whether to determine emission levels or to evaluate the performance of particulate control apparatus, are

(1) Generation of sulfate by oxidation of SO_2 in the impingers. This is also a potential problem in the probe and filter.

(2) Condensation of H_2SO_4 or adsorption of SO_2.

(3) Fractionation of the composite of ash, sulfur oxides, and organic components during passage of the particulate through the sampling apparatus.

(4) Retention of water, especially in those portions of the catch that include free sulfuric acid.

(5) Probable loss of identity of organic materials that are collected simultaneously with the sulfuric acid.

Probe

Comparison runs were made for samples collected using Inconel, 316SS, and Quartz probes. In Tables 8 and 16, the Runs 13, 14, 15, and 23, present data from the comparative runs. The high chromium and nickel contents of the catches collected with metal probes (Runs 13, 14) present clearcut evidence of the accumulation of corrosion products in the probe portion, and, to some degree, in the filter portion at 250 F. In Table 16 the slight increase in sulfur retention by the metal probes, in contrast with the quartz probe, may be a reflection of the increased reactivity of the catch due to these corrosion products.

No clear effect of probe temperature was noted on the nature of the catch, probably because most of the probe was always at duct temperature (about 550 to 750 F) and only the outlet end of the quartz probe was subject to the temperature control at 250 and 400 F.

Analytical results show a varying Si/Al ratio for probe samples, probably because the Si and Al are contributed by both fly ash and coke having different Si/Al ratios.

The experimental Si/Al ratios for the probe samples (see Table 14B) were

Run	Date	Location	Si/Al Mass Ratio
49	10/6/71	E.P. inlet	3.0
50	10/6/71	E.P. outlet	15.0
55	10/8/71	E.P. inlet	0.31
56	10/8/71	E.P. outlet	2.1

These data show a substantial greater Si/Al ratio for samples collected at the precipitator outlet than for those collected at the inlet. (As shown on page III-44) two different coals were fired on the 2 days during which these samples were collected. We assume that the difference in coals accounts for the inlet Si/Al ratio being so greatly different.

Filter

Filter temperatures appear to affect significantly the composition of the filter catch. A 400 F filter temperature resulted in a substantial decrease in sulfur oxide retention compared with that for the 250 F filter (compare Modes F and G in Table 16). Thus, the 250 F temperature of the filter in Mode F retained 41 and 45 percent of the total sulfur catch, whereas the 400 F filter temperature used in Mode G caused only 8 and 24 percent of the total sulfur catch to be retained on the filter. Similarly, the ratio of H_2SO_4/total oxide is less on the filters of Mode G than on those of Mode F. The decrease in sulfur oxide retention by the hotter filter is interpreted to indicate that a considerable portion of the sulfur collected on the filter results from reaction of the particulate with the flue gases, such as condensation of H_2SO_4 and absorption of SO_2, and these reactions are favored at the lower temperature.

Thus, the use of filter temperatures above 250 F during sampling is recommended. The exact temperature to be used for specific studies will have to be determined by future research.

Three filter materials were considered: a silver filter, MSA Glass 1106 BH, and Tissuquartz QAO 2500. Only one run was made using the silver filter and large areas of visible stain on the filter after that run indicated that the anticipated reaction of the silver with the H_2SO_4 vapors had indeed occurred. Because the problem of sulfur oxide retention was an important part of the program planned for this project, no further work was done with the silver filter. The filter is particularly advantageous for electron-probe microanalytical identification of individual particle composition, but this was not emphasized in this program.

After the chemical analyses for early runs showed that the background composition for the glass filter would present analytical problems, detailed comparison of the appearance and performance on the quartz and glass was made. As the separation of the filter catch from the filter itself is usually not practical, the chemical analyses of the catch increases in precision and sensitivity as the filter material becomes more precisely defined. The silver filter is best from this standpoint because it can be dried to constant weight easily and impurity elements are of little consequence in most cases. However, the reactivity of the silver with sulfur led to a preference for the relatively inert quartz filter material.

Comparative surface-area, fiber-diameter, and chemical-analysis data were obtained for the Tissuquartz and the well-established MSA glass filters (see Tables 3 and 4). Both of these filter materials suffer from weighing uncertainties due to their tendencies to pick up water vapor from the air, and they are more difficult to handle than the silver. The Tissuquartz was easily pulverized along with the filter catch in a Polystyrene WigL Bug (Crescent Dental Manufacturing Company) to produce a homogenized mass that was relatively easy to analyze for almost all elements of the catch except Si. Portions of the dry probe catch were analyzed to obtain estimates of this element.

Impinger

The mass of the impinger catch is of overwhelming importance for those flue gas streams with low ash content, as, for example, oil-fired operations or the downstream side of a high-efficiency collector. Following experiments that showed extensive oxidation of SO_2 to sulfate in the impingers, several trials were made to determine what improvements might be made. Trials of modified impinger solutions (adding particulate and also HCl) and modified sample handling (storing samples in liquid-filled bottles rather than in partly filled, oversize bottles) have led to the conclusion that a substantial part of the sulfate created from SO_2 in the impinger portion may be generated during a storage of the sample. The improvement (reduced sulfate sulfur) achieved by sample storage in completely full bottles is illustrated in Table 13.

Sampling Train Modifications

Simultaneous Sampling

As an alternative to the impinger, several trials of the Goksøyr-Ross procedure (G/R) were made and the sulfur oxide catch compared with impinger catch made simultaneously. The details of this comparison, discussed in a later section, are illustrated by the data of Tables 10 and 12.

The comparison shows that, in most cases, substantially less sulfate is found by the G/R procedure than by analysis of the impinger catch. The comparison shows further that the impingers retain on the order of 10 percent or more of the total SO_2 as measured by the G/R procedure and that accurate sulfate estimates from impinger catches will depend on the absence of SO_2 oxidation during collection, sample storage and evaporation, and analysis. The experimental results appear to favor use of a separate train for sulfur oxide measurement.

Use of the G/R Coil in Particulate Sampling

To determine the effect of a separate H_2SO_4 collection on the sulfur oxide retention by the various components of the EPA sampling train, a coil like that used in the G/R procedure was adapted for use with the EPA train and was tried as a means for collecting H_2SO_4 droplets. Results are shown for trials with the coil either before or after the filter holder using flue gas from the Multifuel Furnace, see Table 10 for these trials. The fritted disk normally located at the exit end of the G/R coil was omitted so that it would not interfere with the filter catch. For analysis of these runs, the material caught in the coil was included in the probe catch if the coil was located before the filter, and it was included in the impinger catch if the coil was located after the filter.

Scatter in the results (see Modes H, I, and K in Table 16) made it difficult to compare some of these runs. However, Modes K and H, which differ in the use of the coil before and after the filter, respectively, showed the anticipated result of a lowered sulfur oxide catch in the impingers when H_2SO_4 was removed previously.

In later work, the G/R coil was used in its conventional form as a separate method for SO_3 measurement simultaneously with the operation of the EPA sampling train. Those trials, see page III-35 and Table 10, provided evidence for SO_2 oxidation to sulfate in the impinger portion and so raised the possibility that removal of the strong mineral acid (e.g., H_2SO_4) before the impinger could lead to greater SO_2 solubility in the impinger solution and enhanced opportunity for oxidation to sulfate. Such oxidation effects could be partially responsible for the scatter obtained. For this reason another trial of the coil was made during the field sampling at the pulverized coal-fired boiler at the Edgewater Power Plant. In these trials the fritted disk was included and both the coil and the disk were increased in size compared to the normal G/R coil, to accommodate the higher gas flow rate of the particulate sampler.

Field Trials

Five of the experiments on the pulverized coal-fired boilers at the Edgewater plant at Lorain, Ohio, were planned as an investigation of the effects of sampling method on the oxidation state and material balance of the sulfur oxide portion of the flue gas stream. For this purpose several variations in the sampling train were tried. These included

(1) Use of four impingers, each containing 100 ml H_2O, instead of the usual 2.

(2) Use of a fifth impinger, containing 100 ml of 6 percent H_2O_2, to collect the remainder of the SO_2 in the gas stream effluent from the sampling train. The efficiency of this impinger has not been demonstrated.

(3) Use of a coil, with fritted disk as in the G/R procedure, between filter and impingers. The coil was held at 162 F.

(4) Use of a second filter instead of the coil above, held at 110-120 F.

(5) SO_2/SO_3 collections by the G/R procedure made simultaneously with each of the above experimental trials. These collections were made from an adjacent port but without benefit of traverse.

These modifications had previously been tried using the Multifuel Furnace, see page III-35, or were developed as a result of those trials. These variations in sampling method showed the following effects:

(1) When extra wet impingers were added to the sampling train, as much sulfate is found in the third and fourth wet impingers as in the first two, and the results imply strongly

that the SO_3 catch in the impingers is largely manufactured by oxidation of dissolved SO_2 in that portion of the apparatus.

(2) The SO_2 collected in the fifth impinger (containing H_2O_2) is large and, in most cases, is at least 10 times that found in the water-filled impingers. However, the sum of all sulfur oxides collected with five impingers is not as great as that found by the G/R procedure. The efficiency of the fifth impinger has not been demonstrated; the smaller SO_2 catch in the impinger train may be due either to the inefficiency of this H_2O_2 impinger, or to losses that arise during handling of the other four impinger samples.

(3) The G/R procedure is easy to use and provides reproducible results. A reinvestigation of the experimental methods used by Goksøyr-Ross under stack conditions is recommended.

(4) The G/R coil inserted between filter and impingers collected a substantial portion of the total H_2SO_4 found in that run and was far more effective than the cooler second filter tried in its place in one experiment. In the experiment with the coil, if it is assumed to be as efficient as has been claimed, the sulfate found in the impingers of that run would seem to have been formed by oxidation in the impingers.

(5) When two filters were used in series, the mass loading of the second filter was largely due to sulfur oxides retained there. The mass of fly-

ash oxides on the second filter, excluding sulfur oxides, was small, and the analyses for individual elements were subject to large uncertainties. However, these amounts always exceeded the estimates of oxides found in the impingers. Table 20 extracted from Tables 14A and 14B illustrates this conclusion by comparing the masses of the elements (not oxides) found analytically in the several portions of the catch for four runs.

Sample Handling

In the experiments to determine sulfur (oxide) material balances, the impingers were analyzed as collected and without the preliminary evaporation to dryness usually used. The evaporation step, completed by heating the residues to 212 F, is the source of some potential errors in interpretation of the mass of the particulate due to

- Oxidation of the SO_2 retained in the impinger during its evaporation from the portion of the catch
- Water retention or drying
- Thermal alteration or destruction of the organic portion in the concentrated H_2SO_4 residues that are generated.

It has been seen that substantial, and apprarently arbitrary changes, were produced in the weight of particulate by the choice of drying conditions. The acetone extraction tried on the dried probe and impinger residues (see Table 2) was not valid since it removed inorganic materials and H_2SO_4 that should remain. The weights from this treatment thus should

TABLE 20. IMPINGER AND FILTER CATCH FOR SINGLE AND DOUBLE FILTER EXPERIMENTS, EDGEWATER POWER STATION, LORAIN, OHIO

Run	Portion	Mass, (mg /m^3)	
		Sulfur(a)	Other Elements
49 (dual filter, E.P. inlet)	Probe	99.4	1,301
	Filter #1	21.9	420
	Glassware and filter #2	2.7	1.5
	Impingers #1 and #2	141 (total)	0.15
55 (single filter, E.P. inlet)	Probe	138	1,188
	Filter	27.5	168
	Impingers #1 and #2	298 (total)	0.16
50 (dual filter, E.P. outlet)	Probe	2.0	0.58
	Filter #1	18.7	11.4
	Glassware and filter #2	7.9	2.3
	Impingers #1 and #2	106 (total)	0.07
56 (single filter, E.P. outlet)	Probe	3.3	5.8
	Filter	3.0	6.5
	Impingers #1 and #2	66.0 (total)	0.13

(a) Total sulfur

be too low. The slow and more or less continuous loss of water as the particulate temperature was raised illustrated the difficulty in recognizing when all free water has been removed and only combined water remains. In the absence of a clear-cut distinction between these two water forms, the choices among various drying temperatures was arbitratry. Since free water should be rapidly lost at 212 F, and in view of the weight changes observed, the drying treatment at 210-220 F is now preferred.

Table 11 shows that the solids recovered from the water layers of the probe catch were tan and white solids, similar in appearance to the filter catch. Percentage changes in weight of these solids due to repeated heating and desiccation were quite small (less than 1 percent). However, the impinger water layer and the organic wash leyers were more sensitive to drying procedures and showed variations of 10 percent or more. For these samples from coal-burning operations, the overall variation was not serious since the mass of probe and filter catch represent most of the total catch. However, samples with a substantially lower ratio of ash to sulfur, as from oil-fired operations, would be markedly affected by these variations in weight and could lead to erroneous estimates of control apparatus performance. Similarly, the charring or pyrolysis of the organic portion during the evaporation procedure would inhibit characterization of the metal-organic or toxic components of that portion of the catch.

An improved procedure would seem to be to use separate sample trains for sulfur oxides and for PNA or for certain hazardous heavy metals. In this way the filter system would be used to characterize the inorganic fly-ash particulate only.

Suggested Sampling Procedures

On the basis of observations to date a sampling procedure for examination of the performance of particulate-control equipment might be

a. Use two quartz filters in series at 350-400 F or stack temperature, whichever is higher, so as to minimize reactions of sulfur oxide with the probe and filter catch during sampling and to back up the first filter if defective. The point here is that if a filter is defective, without a back-up there is no way of knowing it, and gross errors can occur.

b. Determine total SO_2 and SO_3 in the gas phase by a procedure, such as that of Goksøyr-Ross, operated simultaneously with the particulate collection.

c. Use special collection trains for components such as PNA and certain hazardous metals present in relatively small concentrations. These trains would be adapted to the most suitable absorption or reaction condition for efficient collection of the component concerned.

d. Attempt material balance by the use of a sufficient scope of analytical methods so that the entire mass of catch is identified according to its chemical characteristics.

The OES and XRF estimates of individual metals have been useful in the present research stages of development of this sampling problem. In future work, the fly-ash portion of probe and filter portions may be suitably measured by difference by correcting the total catch for the mass of sulfur oxides retained, and for the carbon and water contents where necessary. SO_2 and SO_3 emissions would be estimated from separate samples collected for this purpose by a method such as that of Goksøyr-Ross. The impinger catch, if obtained, should be used to obtain estimates of individual metals and organic species not otherwise retained in the probe or on the filters.

Inorganic Ash (less S)

A number of detailed analyses were made of the composition of the fly ash so as to detect any conditions that caused fractionation of this portion of the catch. Such fractionation could be of considerable importance in those cases where heavy metals are involved and especially if the fractionation results in exceptionally high losses of those metals from the sample for any reason.

Differences in particle composition can arise from differences in origin of the particles in the furnace, and from chemical and physical adsorption of components of the stack gases as they cool. Such adsorption processes will have characteristic temperature dependencies that can arise from differences in volatility or from differences in reactivity of the vapors with the existing particulate. These processes of particle formation and reaction, under essentially nonequilibrium conditions in the rapidly cooling stack gases as they leave the furnace, can be expected to produce a mixture of particle compositions and size distributions.

In the initial trials, the analyses of the filter deposits from oil-burning operation of the Multifuel Furnace, see Table 2, were quite similar for the two samples collected on silver, but the interference of the background elements of the glass filter caused considerable scatter in the estimates for the samples from other runs.

Runs 4 and 5, made with silver filter material, show somewhat greater variation in the proportion of vanadium retained than expected from the results for other major elements. The two runs differ mainly in filter temperature, and in this case, the larger vanadium catch was found on the hotter filter. The variation of vanadium retention with change in filter temperature requires further investigation before a real effect can be claimed.

For coal-burning operation, however, variation in particulate composition with changes in sampling conditions and with changes in furnace operation appear real. This is especially noticeable in Tables 14B and 14C for samples collected at Edgewater Power Station. Here, differences in composition for the catch on two filters in series, see Table 14B, and for samples collected from precipitator inlet and exhaust streams, see Tables 14B and 14C, imply composition differences for particles of different size. As the analyses show appreciable coke content for these samples, see Table 19, it is anticipated that the differences in elemental composition are, in part, related to these differences in coke content.

Some fractionation may be anticipated to occur in the precipitator as precipitation efficiencies vary for particles of different size ranges. Thus, using the total mass of inorganic elements found by analysis, but excluding sulfur, the precipitator at the Edgewater plant removed 99.5 percent or better of the relatively coarse material caught in the probe and about 96 to 97 percent of the filter catch portion. For this coal-burning operation, these two portions constitute 99 percent or better of the total catch as determined by analyses.

Most of the mass of particulate is contributed by the elements Na, K, Mg, Al, Si, Ca, Ti, Fe, S, and presumably O. However, a number of heavy elements are presented in amounts that are insignificant compared to the total mass of particulate but which may need to be considered individually for their toxicity contributions. These are identified for coal-burning operations in the analyses of Tables 14B and 14C, and for residual oil fuels in Table 2.

The presence of small concentrations of nitrogen in these samples was revealed by C, H, N analyses, see Tables 9, 17, and 19. Acid extraction of the N from residues listed in Table 9 was interpreted to mean that the nitrogen was present as nitrate. Similarly, the small removal of C by aqueous acid was interpreted to imply the presence of carbonate. In Table 1, the typical flue-gas compositions were examined and it was shown that even very minor retention of the CO_2 and NO_x by the particulate could lead to detectable concentrations of carbonate and nitrate in the particulate. There has not been time in the program to pursue this aspect of the sampling problem. Further attention should be given to investigating the anion compositions of the particulate more thoroughly and especially to the role of halides for their possible effects on particle reactivity, hygroscopicity, and corrositivity.

Sulfur Compounds

The sulfate found in the particulate sample can originate by condensation of H_2SO_4 or by oxidation of SO_2 at any one of several stages in the sampling and analysis procedure. Thus, the sulfate may be the sum of

(1) SO_3 present in the stack gas

(2) SO_3 generated during sampling (here 40 minutes) (In general more SO_3 is generated that is present in the initial gas sampled.)

(3) SO_3 generated during storage of the filter and the impinger and probe solutions under air for transport to the laboratory

(4) SO_3 generated during evaporation of solutions and analysis.

In the work that has been described, attempts have been made to distinguish among these sources and identify the most probable sources of error due to SO_3 generation.

The overall process of concern is

$$SO_2(\text{gas}) \underset{H_2O}{\rightleftharpoons} SO_2(\text{dissolved}) \underset{H_2O}{\rightleftharpoons} H_2SO_3 \rightleftharpoons H^+ + HSO_3^- \underset{1/2\,O_2}{\rightleftharpoons} 2H^+ + SO_4^{-2} .$$

The first step represents the dissolution of SO_2 in water, and the solubility under sampling conditions can be estimated from existing data. Table 21 shows that substantial amounts of SO_2 should be retained in the impinger during sampling. Results of one experiment, Run 41, indicate that the amounts of SO_2 found in the impinger solution corresponded to saturation at a temperature somewhat higher than actually measured. The presence of sulfuric acid and dissolved salts in the impinger solution may contribute to this

TABLE 21. COMPARISON OF CALCULATED SOLUBILITIES[a] FOR SO_2 IN WATER WITH THOSE FOUND IN RUN 41

	Solubilities of SO_2 in H_2O as mg S/100 ml H_2O 32 F	70 F	86 F
Calculated for gas inlet to impingers	20.8	9.7	7.4
Calculated for outlet gas from impingers	15.8	7.4	5.6
Found in impingers, Run 41	2.0 to 5.1; Temperature of gas at outlet = 67 F		

[a] Solubilities calculated using data summarized by L. C. Schroeter, Sulfur Dioxide, Pergamon Press, Inc. (1966), assume solubility varies linearly with pressure of SO_2 gas.

discrepancy. Note also that on page II-12 of this report, it was estimated that dissolved SO_2 concentrations of about 3.1 mg/100 cc could be anticipated from available data for solubility of SO_2 in diluted H_2SO_4 solutions. In any case, the amount of SO_2 dissolved is so large that even minor tendencies for oxidation of the SO_2 could materially alter the estimate of total SO_3.

The fate of this dissolved SO_2 is described by the positions of the subsequent equilibria in the above equation. Available literature(18) indicates that aqueous solutions of SO_2 contain no detectable H_2SO_3 species, and at pH values less than 4 the ionization of HSO_3^- to form SO_3^{-2} is negligible. Thus, essentially only HSO_3^- ions and dissolved SO_2 are present. On this basis, Schroeter(18) writes, for 25 C,

$$K_1 = \frac{(a_{H+})\,(a_{HSO_3^-})}{a_{SO_2}} = 1.72 \times 10^{-2}$$

for the first ionization constant. Hence, for the dilute solutions of concern here it can be assumed that

$$K_1 = \frac{[H^+]\,[HSO_3^-]}{[SO_2]} = 1.72 \times 10^{-2} ,$$

where the brackets represent concentration in moles/liter. If

x = concentration of HSO_3^-,
$a-x$ = concentration of dissolved SO_2, and
a = total concentration of sulfite species,

$$\text{then } \frac{x}{a-x} = \frac{1.72 \times 10^{-2}}{[H^+]} .$$

This relationship has been solved for several sets of values of a $[H^+]$ and the results are presented in Table 22. In this table the concentration of dissolved SO_2 is assumed constant and determined only by the concentration of SO_2 in the gas (which is not specified but is held constant) and by the temperature of the solvent, here 25 C (77 F). Also, the dissolved species are assumed too dilute to substantially affect the equilibrium between $[SO_2]$ dissolved and $[SO_2]$ in gas. $[H]$ is put equal to $[HSO_4^-]$, and "a" assumed = 0.020 moles/liter.

TABLE 22. ESTIMATED CONCENTRATIONS FOR SULFITE SPECIES IN AQUEOUS SOLUTIONS (ASSUMING THE CONCENTRATION OF DISSOLVED SO_2 REMAINS CONSTANT)

	Concentration of Species in Water, solution in moles/liter			
	$[SO_2]$ dissolved	$[HSO_3^-]$	total	
(1) Water solvent, 0.020 m/1, total sulfite	0.0082	0.0118	0.0200	
(2) HCl=0.1 m/1; $[SO_2]$ dissolved same as (1)	0.0082	0.0015	0.0097	large amount of acid
(3) $H_2SO_4 \approx 0.001$ m/1; $[SO_2]$ dissolved same as (1)	0.0082	0.0114	0.0196	small amount of acid

For the cases considered, the concentration of total sulfurous acid species can vary by a factor of two or more as a result of the presence of strong mineral acid in the impinger solution. Of somewhat greater significance is the eightfold range of HSO_3^- in concentrations that might be produced by acid addition since the kinetics of oxidation are related to this quantity. Consideration of the rate of oxidation requires closer attention to a number of other factors that are discussed below.

Many factors can influence the rate of that oxidation and predictions of such rates are highly speculative. In the laboratory and using carefully purified solution, the oxidation process has been observed to be a chain reaction process in which the rate of disappearance of total sulfurous acid species (S_t) by oxidation is expressed by

$$\frac{-d\ S_t}{dt} = \frac{g\ [HSO_3^-]}{\sqrt{H^+}} \quad ,$$

where $[HSO_3^-]$ = concentration of bisulfite ion

$[H^+]$ = concentration of hydrogen ion

g = reaction rate constant, the value is dependent on O_2 partial pressure for well stirred systems.

The lowered rate of oxidation found at low pH's is the consequence of the hydrogen ion effect on that rate equation. Hence, as the pH changes in the range from 4 to 1 a hundredfold decrease in oxidation rate is predicted even if no change in $[HSO_3^-]$ is produced. This effect is responsible, at least in part, for the belief that the oxidation ceases at low pH values. However, for the long periods of storage that are typical for impinger samples collected in the field, such rates can be very significant. The review and summary of available data by Schroeter indicates that the rate constant for the uncatalyzed reaction

$$HSO_3^- + 1/2O_2 \rightarrow H^+ + SO_4^{-2} \quad ,$$

is 2.0×10^{-8} (moles/liter)$^{1/2}$/second in a well-stirred reactor. In the impinger, the H^+ ion concentration is controlled by the mixture of acid and ash ingredients which tend to buffer the mixture. Measured pH values have generally been in the range pH = 2 to 3 after return of impinger samples to the laboratory. Assuming a pH of 2 for the impinger sample, the above first order reaction corresponds to a half-life (i.e., time for half of the existing S_t to be oxidized to SO_4^{-2}) of slightly less than 10 hours. Higher pH values will yield higher oxidation rates and the absence of stirring will lead to lower rates of oxygen dissolution and, hence, slower oxidation.

This calculated half-time rate, for an uncatalyzed system, indicated that large amounts of SO_3 may be produced overnight from typical impinger solutions. Further, shortening of the storage period is not a general solution to this problem since 10 percent of the existing SO_2 would be oxidized in about 1 to 2 hours. This means that the SO_2/SO_3 determination must be carried out immediately unless oxygen can be rigidly excluded during storage. The storage of aliquots of samples in liquid-filled bottles at Edgewater Power Station was done for this reason. A better alternative might have been to flush the sample with an inert gas, such as Freon, using the readily available 1-pound containers of that gas.

A further alternative would be to inhibit the oxidation by chemical means: manitrol, isopropylalcohol, and glycerine have been used for this purpose.(18) Trials of such materials will require demonstrations that the inhibition has been suitably completed over long periods of time (days), and also will require assurances that the addition has not interfered with analyses planned for other organic elements and organic species.

These considerations made it appear probable that SO_2 oxidation would be encountered in the impinger train. Therefore, several trials were planned to evaluate the degree of this problem. The two series of trials made using the Multifuel Furnace under coal-fired operation (see Table 10) and the field trials at Edgewater Power Station (see Table 12) utilized a number of variations in sampling trains and sampling conditions. These included the use of extra impingers containing water, in series with the usual two, G/R coil insertion in series with the conventional parts of the sampling train, and comparison collections of SO_2 and SO_3 using the G/R procedure operated simultaneously with the sampling train. In practically all cases, the amount of sulfate sulfur collected in the impingers substantially exceeded that found by the G/R procedure. Further, the sulfate sulfur remained high even in the third and fourth impingers so that the distribution of sulfate strongly implied that SO_2 oxidation was occurring in the impinger train.

The amount of SO_2 retained by the cold water in the impinger has been shown to be high and consistent with available solubility data (see Table 21). Retention of SO_2 approached 10 times the amount of SO_3 found. Thus, the oxidation of only a minor part of the SO_2 retained by the impingers would produce the substantially larger sulfate catch found there in comparison with the G/R procedure.

The kinetic calculations fo SO_2 oxidation indicate, however, that the amount of oxidation that occurs during sample handling and storage may be more serious than that occurring during the 40-minute sampling period.

The trials of buffered impinger solution at pH = 5.5 (see Table 10), doubled both the SO_2 and SO_3 retention in one series of trials. In that same series, a comparison run with filter-catch particles added to the impingers further increased the SO_3 found. A subsequent trial of filter-catch material from the Edgewater Power Station added to the impinger did not produce a similar increase, however. The relatively large coke content of this filter catch material may have been responsible for this difference but no experimental confirmation is available.

It was anticipated that a highly acid solution would not absorb much SO_2. However, lowering of the impinger pH to between 1.1 and 1.5 produced only a minor decrease in SO_2 retention over that found in a comparison run (see Table 10) but the amount was substantially below that found in earlier trials using the same furnace (compare Runs 38, 41, 42, 43 in Table 10). These trials of the effect of lowered pH are thus regarded as inconclusive.

The effect of changes in filter temperature (see Tables 8 and 16) are interpreted to mean that a substantial part of the sulfur found on the filter is the result of condensation and reaction with the gas phase. The larger sulfur oxide catch at lower filter temperature suggests reactions following adsorption, and the relatively large fraction of sulfite sulfur found on the filters of Table 12 indicate that SO_2 is involved in this adsorption. The discussion of the energetics of adsorption, see page II-12 et seq., indicates that this is not a surprising result, and the work of Ketov(19) shows that chemical interaction of gaseous SO_2 is observed with alkaline earth oxides, e.g., CaO, over the temperature range 600 to 1800 F. Thus, the mass of the filter catch may be anticipated to be high as a result of SO_2 and SO_3 interactions that occur during collection. The use of filter temperatures of about 400 F was found to be advantageous since the sulfur retention was less than that found on filters held at the more conventional 250 F temperature.

Similar observations of oxidation of SO_2 have been reported on glass filters as a result of the alkali content of the glass.(6) A similar test of the quartz filter has not been made; however, since the quartz does not contain any appreciable amount of alkali oxides, its activity, if any, in catalyzing such oxidations may be more dependent on surface contamination by such material during use, for example, by the fly ash.

V. RECOMMENDATIONS FOR FUTURE WORK

The work done under the present contract has served to identify several areas for work to supplement the study that has been made of the chemical composition of particulate. These areas for further research all relate to the observation that some fractionation of particulate can occur in the particulate control apparatus as well as in the furnace or boiler itself, and studies will be needed to establish a basis for measurement of control for each of the important classes of material. Among these areas for further research are

(1) Sampling and analysis of small particles that may penetrate the filter

(2) Sampling and analysis of anions, especially halides, nitrates, and carbonates

(3) Study of the chemical state of selected heavy metals and identification of sampling difficulties for each, especially for Hg, Ba, Sb, Pb, As.

(4) Study of special sampling conditions that are generated by scrubber-type particulate control apparatus

(5) Demonstration of a valid sampling method for emissions from presently used particulate control equipment in major industries.

It is recommended that a continuation of the study of SO_3 sampling should start with a study of G/R procedure under stack sampling conditions. Ultimately, agreement must be obtained between the analytical results of any candidate method and known values. Because a referee sampling method for SO_3 does not exist, the demonstration must be based on known additions to stack mixtures. Difficulties revealed in the present program are believed to indicate that each experimental collection must attempt to identify all sulfur in the stream being sampled for comparison with the inlet stream content so that coincidental adsorptions and chemical conversions of SO_2 to SO_3 may be identified. It is suggested that a permeation tube for SO_3 might be possible using oleum in thin-walled tubing.

Reinvestigation of the G/R coil leads logically to the question of small-particle collection, in that the efficiency of the coil must depend on the efficiency for collection of all H_2SO_4 particles that exist in the stream under coil conditions. In an extension of the use of that coil, it might be operated under conditions such that appreciable supersaturation of water vapor is generated in the stream so that the small particles will serve as condensation nuclei in the coil. The growth of particle size obtained in this way may prove to be an efficient basis for collection of the smaller particles and, if successful, could also serve for estimation of the sulfate content of ambient air samples.

Chemical problems relating to the identification of halides (e.g., chloride ion) nitrates, carbonates, and heavy metal compounds must be studied from a twofold point of view: first to identify these accurately in minor concentration in existing particulate, and second to measure emissions of these in gases that also contain particulate for those cases where the total emission level is important.

Conceivably, these studies will identify methods to supplement the existing sampling train, and these must be tried under comparative conditions in industrial applications where particulate and emission control equipment is used. In this connection, the special problems generated by the use of scrubber-type control apparatus should be studied immediately so that the observations may be used to guide the other research areas discussed here.

VI. ACKNOWLEDGEMENTS

The authors of this report have been assisted at many points in the research by helpful comments, suggestions, and active experimental support in the course of the project. Of particular help were:

Environmental Protection Agency

John O. Burckle	Original Project Officer
James A. Dorsey	Program Coordinator
Robert L. Larkin	Second Project Officer
D. Bruce Harris	Third Project Officer

Battelle-Columbus

David W. Locklin	Project Director
John F. Foster	Senior Project Leader
William M. Henry	Chief, Environmental and Materials Characterization Division
Richard E. Heffelfinger	Associate Chief, Environmental and Materials Characterization Division
Earl J. Schulz	Senior Technologist
Clarence McComis	Master Technician
Dan L. Chase	Senior Chemist
Bernard Paris	Research Chemist
John H. Faught	Senior Technician
William G. Keigley	Technician
Paul D. Miller	Associate Fellow
Paul R. Webb	Senior Technologist

The management of the Ohio Edison Company and their staff at the Edgewater Plant were significantly helpful in the field investigation.

APPENDIX

A. CONVERSION OF SO_3 TO H_2SO_4

B. WET CHEMISTRY METHODS FOR SULFUR COMPOUNDS

C. FILTER EFFICIENCY MEASUREMENT

D. FIELD TEST SAMPLES FROM OTHER EPA CONTRACTORS

E. KINETICS OF SO_2 OXIDATION

F. REFERENCES

V-2

APPENDIX A

CONVERSION OF SO_3 TO H_2SO_4

To answer the question of how much of the SO_3 in flue gas is present as H_2SO_4, consider the following equilibrium:*

$$H_2SO_4(g) \rightleftharpoons SO_3(g) + H_2O(g)$$

$$K = \frac{(H_2O)\ (SO_3)}{(H_2SO_4)} \qquad \text{(moles vapor/}\ell\text{)}$$

$$\log_{10}K = \frac{-22850}{4.571T} + 0.75\ \log_{10}T - 0.00057T + 4.086.$$

(over the temperature range 598 to 756 K)

First calculate position of the above equilibrium at the highest temperature of interest, 400 F (477 K) assuming the above expression for $\log_{10}K$ is valid:

$$\log_{10}K = 10.480 + 2.009 - 0.272 + 4.086$$

$$= -4.657$$

so at 400 F $\quad K = 0.220 \times 10^{-4} = \dfrac{(H_2O)\ (SO_3)}{(H_2SO_4)}$

at 1 atm, $0^\circ C$, ideal gas $= \dfrac{1}{22.40}\ m/\ell = 0.0446\ m/\ell$

at 1 atm, $477^\circ K$ ideal gas $= \dfrac{273}{(477)\ (22.40)} = 0.0256\ m/\ell$

In the Typical Gas Composition, Table 1, page II-2, $H_2O = 4\%$,
so $H_2O = 0.04 \times 0.0256 = 1.024 \times 10^{-3}\ m/\ell$.
Similarly, $SO_3 = (3.0 \times 10^{-5} \times 2.56 \times 10^{-2} - X) = (7.7 \times 10^{-7} - X)$ moles/ℓ
$H_2SO_4 = X$ moles/liter

$$0.220 \times 10^{-4} = \frac{(1.02 \times 10^{-3})\ (7.7 \times 10^{-7} - X)}{X}$$

$X = 7.51 \times 10^{-7}$; or 97.8% of SO_3 is H_2SO_4.

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Similarly, at 300 F (422 K);

$$\log_{10}K = 11.846 + 1.970 - 0.241 + 4.086$$

$$\log_{10}K = -6.031$$

$$K = 0.935 \times 10^{-6}$$

at 1 atm, 422 K, ideal gas is $0.446 \times \frac{273}{422} = 0.289$ m/ℓ

$$H_2O = 0.40 \times 0.0289 = 1.16 \times 10^{-3} \text{ m/ℓ}$$

$$H_2SO_4 = X \text{ m/ℓ}$$

$$SO_3 = 3 \times 10^{-5} \times 0.0289 - X = (8.66 \times 10^{-7} - X) \text{ m/ℓ}$$

$$0.935 \times 10^{-6} = \frac{(1.16 \times 10^{-3})\ (8.66 \times 10^{-7} - X)}{X}$$

$$(0.935 \times 10^{-6})X = 1.04 \times 10^{-9} - (1.16 \times 10^{-3})X$$

$$X = \frac{1.004 \times 10^{-9}}{1.16 \times 10^{-3}} = 0.866 \times 10^{-6}$$

at 300 F $H_2SO_4 = 8.66 \times 10^{-7} \approx 100\%$ of SO_3 is present.

Hence, SO_3 essentially exists as H_2SO_4 over the entire range of conditions of interest, if the time is sufficient to allow equilibrium of the hydration.

APPENDIX B

WET CHEMISTRY METHODS FOR SULFUR COMPOUNDS

Sulfate Sulfur

Tap sample into beaker, dilute to 200 ml and acidify with 1:1 HCl. Boil to expel H_2S. (Boil for 15 minutes at least). Add to 10 ml of 10 percent $BaCl_2$ solution to boiling solution (add slowly). Let stand overnight. Filter and wash the $BaSO_4$ until Cl free. Place in crucible. Char and heat to 900 C at least an hour. Weigh $BaSO_4$ and calculate as SO_4 sulfur.

Total Sulfur

Tap sample into beaker containing bromine and 1:1 HNO_3 acid. Let stand 1/2 hour. Heat gently until bromine is expelled (use boiling rods). Add 20 ml HCl and heat until HNO_3 appears gone. Cool sample, wash down the sides of the beaker, add 10 ml HCl and take down to near dryness. Repeat last step. Cool sample, add 10 ml 1:1 HCl to dissolve salts and dilute to 200 ml. Bring to a boil and ppt. sulfur by adding 10 ml of 10 percent $BaCl_2$ solution. Let stand overnight. Filter and wash until Cl free. Place in crucible. Char and heat to 900 C for at least an hour. Weigh as $BaSO_4$ and calculate as sulfur.

APPENDIX C

FILTER EFFICIENCY MEASUREMENT

by Paul R. Webb

The efficiency of quartz-fiber filters (Tissuquartz 2500 QAO) and glass fiber filters (MSA 1106B) were compared at a face velocity and particle diameter which would be comparable to those conditions generally expected during use.

Figure 1C is a sketch of the sampling arrangements. For each experiment, two 47-mm-diameter disks were cut from a common quartz fiber or glass-fiber filter sheet and the two identical filter disks placed in series in the primary and backup positions of a 47-mm Millipore filter holder. The filter holder inlet was inserted through the wall of a 16-cubic-foot plastic sphere.

The filtering efficiencies of the filters were expected to be on the order of 99.99 percent, therefore, the sensitivity of the technique used for detecting particle penetration was necessarily such that about one part in one million could be detected. This sensitivity was obtained by generating a fluorescent aerosol, and using a fluorophotometer to determine the relative fluorescent concentrations collected on the primary and backup filters. Under the conditions used in this study fluorescent units are proportioned to the mass of fluorescent dye particles in the sample. Fluorescent units (F.U.) are defined as the product of the fluorophotometer reading and total sample volume.

The sampling continued for approximately 4 hours with additional particles being sprayed into the sphere every hour.

At the end of the sampling period, the two quartz filters were removed from the holder and each placed into separate beakers. The collected particle samples were then dissolved in ethyl alcohol and the relative particle mass on each filter determined with a fluorophotometer.

The fluorescent aerosol was generated from a pressurized container having the following constituents:

Freon 12	360 g
Fluorescent Dye	0.1 g
Toluene	1.0 ml.

Atomization of this mixture into air under the experimental conditions produces an aerosol of solid dye particles. The particle size distribution of this aerosol, shown in Figure 2C, was determined with the aid of a Battelle cascade impactor.

The fluorescent aerosol was sprayed into the sphere for only a few seconds in order to maintain relatively low particle concentrations. High particle concentrations tend to cause agglomeration of the particle

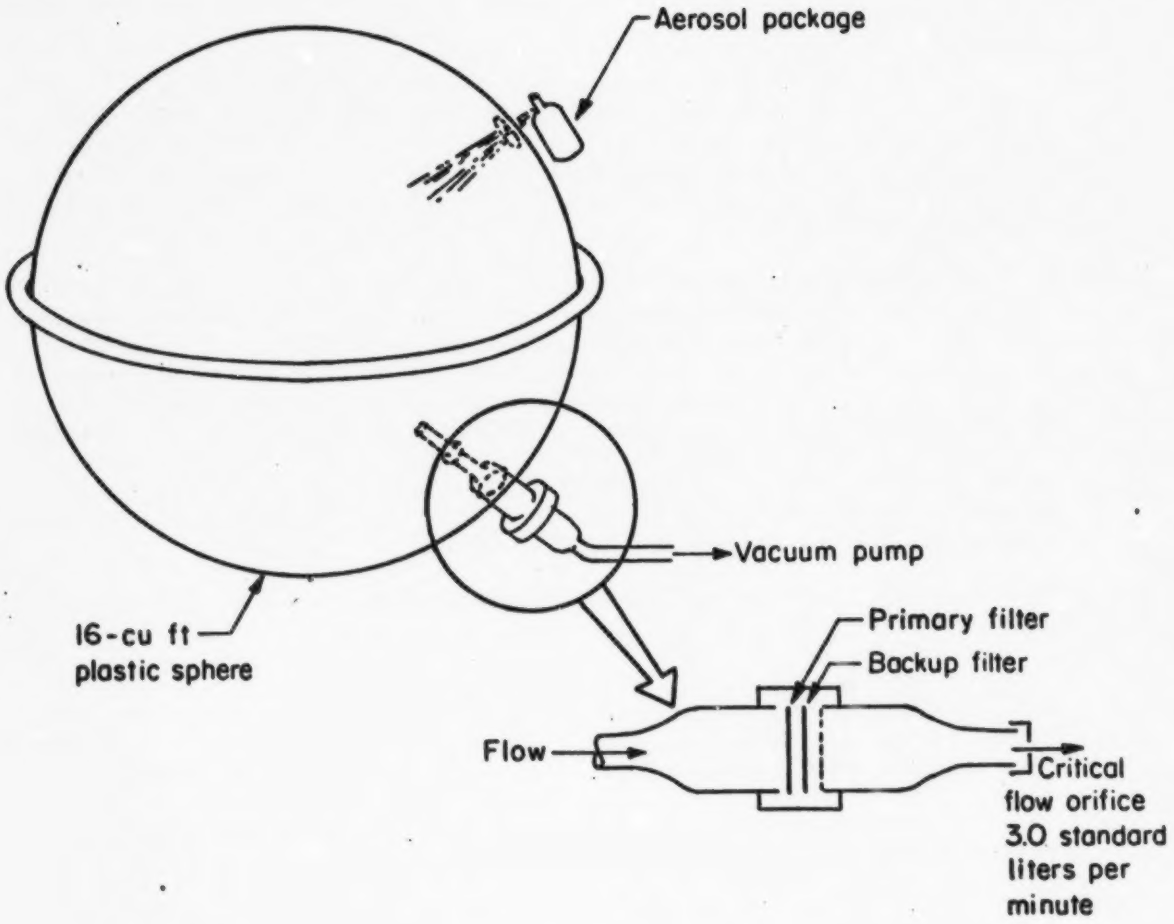
Aerosol package
Vacuum pump
16-cu ft plastic sphere
Primary filter
Backup filter
Flow
Critical flow orifice 3.0 standard liters per minute

FIGURE 1C. SKETCH OF SAMPLING ARRANGEMENTS

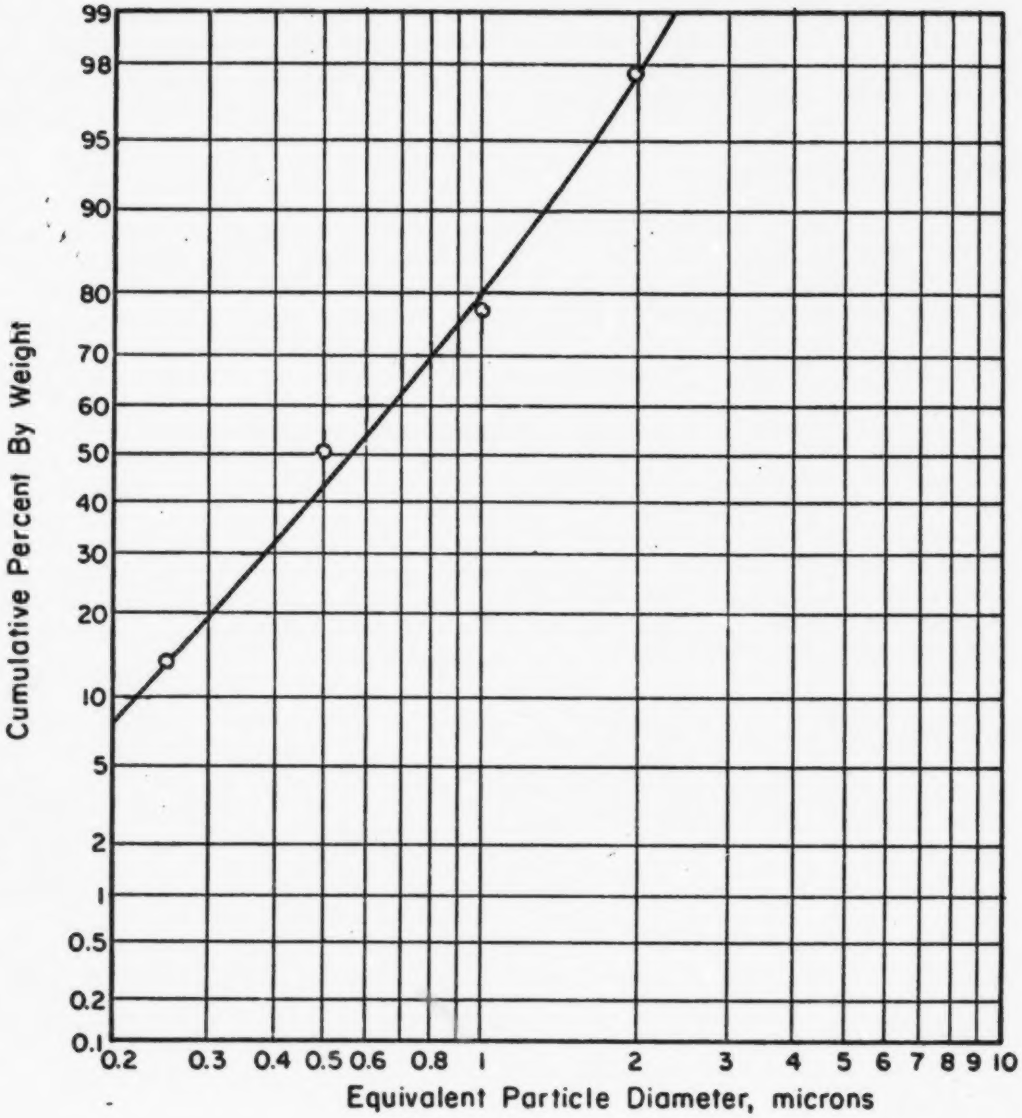

FIGURE 2C. PARTICLE SIZE DISTRIBUTION

and, hence, changes in the particle size distribution. The concentration of particles in the sphere was less than 10^5 particles/cm^3 and well below the concentration of about 10^8 particles/cm^3 where agglomeration would be expected to become significant.

Results and Discussion

The efficiency of any filtering media is a function of the face velocity and particle diameter. A direct comparison of quartz-fiber filters and MSA 1106 BH glass-fiber filters has been made using the fluorescent-dye method at a face velocity of 5.21 cm/sec and a mean particle diameter of 0.55 μ. The average efficiencies at these conditions as can be seen in Table 1C were 99.9932 percent and 99.9909 percent, respectively.

For comparison with the standard DOP penetration tests, the data of Lockhart, Patterson, and Anderson(1) for the MSA 1106B glass-fiber filters have been extrapolated to a face velocity of 5.2 cm/sec where the efficiency would be expected to be about 99.986 percent. A similar extrapolation of the data of Smith and Surprenant(2) would indicate an efficiency in excess of 99.99 percent for the glass-fiber filters at this face velocity. The differences in these extrapolated efficiencies for DOP particles with 0.3 micrometer diameters and the experimental results presented herein can be attributed to differences in the particle sizes.

The objective of this study was to obtain comparative efficiencies and from the results it can be concluded that the quartz-fiber filters are as efficient as the MSA 1106B glass-fiber filters and can be used effectively as a filtering media.

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(1) Lockhart, L.B., Jr., Patterson, R.L., Jr., and Anderson, W.L., "Characteristics of Air Filter Media Used for Monitoring Airborne Radioactivity", NRL Report 6054 (1964).

(2) Smith, W.J., and Suprenant, N.F., "Properties of Various Filtering Media for Atmospheric Dust Sampling", Proceedings of the ASTM, Vol. 73, pp 1122-1135 (1953).

TABLE 1C. COMPARISON OF QUARTZ-FIBER FILTERS AND MSA 1106B GLASS-FIBER FILTERS USING FLUORESCENT DYE METHOD AT FACE VELOCITY OF 5.21 CM/SEC AND MEAN PARTICLE DIAMETER OF 0.55 μ

Filter	Test No.	Primary Filter, F.U.	Backup Filter, F.U.	Penetration, percent	Efficiency, percent
Quartz	1	18.00×10^6	0.0012×10^6	0.0067	99.9933
Quartz	2	12.95×10^6	0.0010×10^6	0.0070	99.9930
				Average	99.9932
MSA1106B	3	11.122×10^6	0.0012×10^6	0.0108	99.9872
MSA1106B	4	19.46×10^6	0.0015×10^6	0.0077	99.9923
				Average	99.9908

APPENDIX D

FIELD TEST SAMPLES FROM OTHER EPA CONTRACTORS

Table 1D shows the analytical results for the A, C, and D fractions of the samples submitted by W. J. Basbagill at the request of the Sponsor. The samples are further identified in Table 4 of the Seventh Monthly Progress Report. The determinations were metallic concentration by optical emission spectrography on two of the fractions; total carbon combustion on all fractions; total acid as H_2SO_4; and total sulfur by the gravimetric method.

Carbon and total sulfur determinations were done only on fractions containing sufficient quantities of deposits. The total acid content as H_2SO_4 of the fractions was determined by titrating a water solution of the residues with standardized NaOH. Acid was found in all fractions. Several fractions which did not show any weighable residue, but showed the presence of titrated acid, could not be reported on a percentage basis. Total sulfur was determined from these solutions by the gravimetric method.

TABLE 1D. CHEMICAL ANALYSES OF FRACTIONS OF FOUR STACK SAMPLES

	EPA							Weight Percent of Total Sample						
Sample	No.	Fraction	Container Number	Weight Milligrams	Total S	Acid, as H_2SO_4	C	B	Si	Mg	Fe	Al	Ag	Ca
Detroit Edison	-	A	20	0	(a)	(b)	(a)							
Detroit Edison		C	9	229.	10.	30.	0.2	0.9	.2	<0.01	.02	<0.01	<0.01	.04
Detroit Edison		D	21	0	(a)	(b)	(a)							
Illinois Power	2E	A	35	0.6	(c)	83.	(a)							
Illinois Power		C	15	83.	17.	50.	0.8							
Illinois Power		D	32	0.4	(c)	20.	(a)							
Illinois Power	2W	A	26	21.6	15.	39.	16.							
Illinois Power		C	11	236.	12.	35.	<0.1	.02	.02	<0.01	.02	.02	<0.01	.1
Illinois Power		D	25	0	(a)	(b)	(a)							
Kansas P & L	2A	A	2a/5	26.	1.0	0.3	79.							
Kansas P & L		C	6	85.	22.	67.	0.3							
Kansas P & L		D	5	14.5	16.	45.	15.0							

(a) Not determined.

(b) Acid, as H_2SO_4, found as milligrams were:
DE A & D - 0.61 mg and .03 mg, respectively,
IP - 2W-D - 0.04 mg.

(c) Determined, but values are suspect because of low quantity of residue.

APPENDIX E

KINETICS OF SO_2 OXIDATION

Schroeter has summarized the data for the rate of oxidation of SO_2 in water solution for the case of a well-stirred solution saturated with O_2 at normal air partial pressure. The rate of oxidation of SO_2 in water solution is quite sensitive to the presence of other ingredients that can either catalyze or retard the rate of this reaction. Schroeter's data can be used to make an order of magnitude estimate of the rate and amount of SO_2 oxidation to sulfate in impinger solution both during the period of sampling of sulfurous gases and during sample storage.

For this purpose we envision the following set of reaction processes:

(1) $SO_2 \text{ (gas)} \underset{\substack{H_2O \\ \text{solvent}}}{\rightleftarrows} SO_2 \text{ (dissolved)}$

(2) $SO_2 \text{ (dissolved)} + H_2O \text{ (liquid)} \rightleftarrows H_2SO_3$

(3) $H_2SO_3 \rightleftarrows H^+ + HSO_3^- \rightleftarrows 2H^+ + SO_3^{-2}$

(4) $HSO_3^- + 1/2\ O_2 \rightleftarrows H^+ + SO_4^{-2}$.

Reaction 1 represents the equilibrium between gaseous SO_2 and dissolved SO_2 and this equilibrium is assumed to be maintained during the sampling period. Reaction 2 represents the hydration of SO_2 to form sulfurous acid in the aqueous solution; this acid ionizes according to the processes of Reaction 3. Available evidence indicates that aqueous solutions of SO_2 contain no detectable amounts of unionized acid, i.e., H_2SO_3, and according to the equilibrium data at pH values below 4, the amount of SO_3^{-2} is negligible compared to HSO_3^-. Thus, only HSO_3^- and dissolved SO_2 are present in the assumed impinger solution initially.

We shall consider two cases:

1. Oxidation in the impingers during sampling. The passage of the sample gas through the impinger maintains the solution in a well-stirred condition, and the continuing supply of fresh SO_2 (2000 ppm) and O_2 (at 4%) is assumed to maintain the solution at saturation levels for the operating temperature. We shall assume that the liquid in the first impinger is warmer than that in the other impinger and put it at 25 C for convenience in calculation.

2. Oxidation during storage in the presence of a moderate amount of air, sufficient to maintain the O_2 level of the stored sample. Assume 25 C, normal air-O_2 level.

The review and summary of available data by Schroeter indicates that the rate of disappearance of total sulfur dioxide species (by oxidation),

$$-\frac{d\,S_t}{dt},$$

for the uncatalyzed reaction is

$$-\frac{d\,S_t}{dt} = \frac{g\,[HSO_3^-]}{[H^+]^{1/2}}, \qquad (1)$$

where

$[HSO_3^-]$ = concentration of HSO_3^- ion

$[H^+]$ = concentration of H^+ ion

g = reaction rate constant dependent on O_2 concentration in solution and pH for a well-stirred system.

If we assume $g \approx k\,[O_2]$ then

$$-\frac{d\,S_t}{dt} = g\,\frac{[HSO_3^-]}{[H^+]^{1/2}} \approx \frac{k\,[O_2]\,[HSO_3^-]}{[H^+]^{1/2}}.$$

Then, for a specified O_2 concentration and pH, the rate becomes

$$-\frac{d\,S_t}{dt} = k_1\,[HSO_3^-]$$

which is a pseudo first-order rate expression.

For Case 1, $[S_t]$ does not vary with time since the fresh gas is continually replacing any portion of dissolved SO_2 and HSO_3^- that is lost by oxidation. In that event

$$d\,(\text{sulfate}) = -d\,S_t = g\,\frac{[HSO_3^-]}{[H^+]^{1/2}}\,dt.$$

Since we assumed 4% O_2, $g \approx \frac{2.0 \times 10^{-6}}{5}$ or $g = 0.4 \times 10^{-6}\,\left(\frac{\text{mole}}{\text{liter}}\right)^{1/2}\,\text{sec}^{-1}$, and $[HSO_3^-]$ at 25 C is expected to be about 3.0×10^{-3} molar for 2000 ppm SO_2 in the sample gas stream. Thus,

$$(\text{sulfate})_{\text{total}} = \frac{3.0 \times 10^{-3}}{[H^+]^{1/2}}\,(0.4 \times 10^{-6})\,t.$$

If sample collection is carried out for 1 hour, t = 3600 seconds, then

pH	$[H^+]^{1/2}$	Sulfate Formed moles/1	 mg S/100 ml
2	0.1	4.3×10^{-5}	0.14
4	0.01	4.3×10^{-4}	1.4

We thus expect somewhere between 0.1 and 1.4 mg of sulfur may be retained in the first impinger of our assumed sample because of sulfate formation during sampling.

For Case 2, there is no replenishment of SO_2 during storage so that as sulfate is formed the concentration of sulfurous acid species in solution decreases with time. From the above we have

$$-\frac{d\,S_t}{dt} = k_1\ [HSO_3^-]\ ,$$

where k_1 is a function of dissolved O_2 concentration, temperature, and pH. At any time t, and at pH<4, $[HSO_3^-] \approx S_t = a - x$, where a is the initial concentration of sulfurous acid species and x is the amount oxidized at time t. Then

$$-\frac{d\,S_t}{dt} = \frac{dx}{dt} = k_1\ (a-x) \text{ and so } k_1\ t = \ln_e \frac{a}{a-x}\ .$$

This is the expression for a first-order reaction and it is characterized by the fact that the time for half of the sulfurous acid species to be oxidized is a constant regardless of the magnitude of the acid concentration.

Thus, $t_{1/2} = \frac{0.693}{k_1}$, similarly, $t_{1/10} = \frac{0.105}{k_1}$. For $k_1 = \frac{g}{[H^+]^{1/2}} = \frac{2.0 \times 10^{-6}}{[H^+]^{1/2}}$

we have

pH	$[H^+]^{1/2}$	$t_{1/10}$	$t_{1/2}$
2	0.1	5.3×10^3 sec (1.5 hr)	3.46×10^4 sec (9.6 hr)
4	0.01	5.3×10^2 sec (0.15 hr)	3.46×10^3 sec (0.96 hr)

Thus, for solutions obeying this kinetic expression, 10 percent of the dissolved SO_2 might be oxidized in 0.15 to 1.5 hr and 50 percent in about 1 to 10 hr For samples stored in half-filled bottles, in air, ample O_2 is usually present but the rate will be less than the above in proportion to the actual dissolved O_2 level maintained. For 2000 ppm SO_2 t water solution may contain about 10 mg S as SO_2/100 ml, i.e., per impinger, at 20 C; and about 20 mg S as SO_2/100 ml at 0 C, oxidation of even 1/10 of this SO_2 is usually of importance. The above estimate that 10 percent oxidation may occur in 9 to 90 min with adequate stirring raises the possibility that sample storage for that period of time will be sufficient to produce 1 to 2 mg S as sulfate if stored in contact with air. Agitation of samples during storage will probably not be sufficient to maintain this rate, but storage periods commonly are much longer, e.g., overnight and sometimes for days.

The above calculation should not be taken as proof that such oxidation must occur in each case, but rather that ample opportunity exists for such errors to arise. First of all, the rate calculations apply to SO_2 dissolved in pure water and other ingredients are known to both catalyze and inhibit such oxidation. Further, sample handling methods will strongly influence the result. A sample stored in a closed impinger will retain most or all of the dissolved SO_2 in the presence of flue gases containing on the order of 4 or 5 percent O_2, whereas a sample poured into a graduate for volume estimations (as in moisture determination) will be exposed to higher O_2 saturation levels but may be substantially outgassed of the dissolved SO_2 originally retained in the impinger liquid. Similar oxidation effects should occur during sample evaporation in open dishes. Storage of samples in half-filled or in completely filled bottles will further affect the result.

Since most of these variations in procedure are not closely regulated, nor is the period of storage between field sampling and analysis, errors of the magnitude shown by the calculations may occur. These errors are of great importance since the "manufactured" sulfate can be a substantial part of the total particulate collected from a low-particulate loading such as for samples collected downstream of precipitators.

APPENDIX F

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